

INFORMATION TO USERS

This dissertation was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.
2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.
3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again — beginning below the first row and continuing on until complete.
4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

University Microfilms

300 North Zeeb Road
Ann Arbor, Michigan 48106
A Xerox Education Company

72-23,211

MARCUS, Lawrence Harvey, 1942-
AN INVESTIGATION OF ALKALI METAL DERIVATIVES OF
GERMANE AND SOME NEW FLUOROSILYL COMPOUNDS.

Carnegie-Mellon University, Ph.D., 1972
Chemistry, inorganic

University Microfilms, A XEROX Company, Ann Arbor, Michigan

THIS DISSERTATION HAS BEEN MICROFILMED EXACTLY AS RECEIVED.

Reproduced with permission of the copyright owner. Further reproduction prohibited without permission.

Carnegie-Mellon University

CARNEGIE INSTITUTE OF TECHNOLOGY
AND
MELLON INSTITUTE OF SCIENCE

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

TITLE AN INVESTIGATION OF ALKALI METAL DERIVATIVES OF GERMANE
AND SOME NEW FLUOROSILYL COMPOUNDS

PRESENTED BY LAWRENCE H. MARCUS

ACCEPTED BY THE DEPARTMENT OF CHEMISTRY

Charles H Van Dyke May 1, 1972
MAJOR PROFESSOR DATE

Albert R. Caritto, Jr May 1, 1972
DEPARTMENT HEAD DATE

APPROVED BY THE COLLEGE COUNCIL

Osmond 5/2/72
DEAN DATE

PLEASE NOTE:

Some pages may have
indistinct print.

Filmed as received.

University Microfilms, A Xerox Education Company

To my wife, Judy

ACKNOWLEDGEMENTS

The author would like to gratefully acknowledge the assistance of Dr. Charles H. Van Dyke in all aspects of this research. His patience and guidance have helped make this dissertation possible. Thanks are extended to the Department of Chemistry at Carnegie-Mellon University for their support through most of this research in the form of Teaching Assistantships and an NDEA grant. Thanks are also given to the Petroleum Research Fund for their financial assistance.

Gratitude is expressed to Mr. James Boal for his assistance in mass spectrometry, to Mr. Joseph Zagorec for his excellent aid in glassblowing and to the author's fellow graduate students for all their help.

TABLE OF CONTENTS

	<u>Page</u>
I. Introduction	
A. Present Research-----	1
B. General Aspect; of the Group IVB Elements and Their Compounds-----	2
C. Background Information Concerning Reactions Investigated in the Present Research Project-----	12
II. Experimental	
A. Apparatus and Techniques-----	24
B. Reagents and Starting Materials-----	37
C. The Preparation and Characterization of Some New Organogermanes-----	41
D. The Reaction of Alkali Metal Derivatives of Germane with Vinyl Bromide, 1,2-Dichloroethene, 1,1,1-Trifluoro- 2-chloroethane and Chloroacetonitrile-----	79
E. The Fluorination of the Silicon-Hydrogen Bond by Phosphorus Pentafluoride-----	83
F. The Attempted Preparation of Psuedohalogen Derivatives of Silylmethane-----	111
G. The High Resolution Proton Magnetic Resonance Spectra of 3-Germylpropene, 3-Silylpropene and 3-Monofluoro- silylpropene-----	115
III. Discussion	
A. The Use of Alkali Metal Derivatives of Germane in the Synthesis of Organogermanes-----	135
B. The Reaction of Phosphorus Pentafluoride with Selected Silicon Hydrides-----	148
C. The High Resolution Proton Magnetic Resonance Study of Allylic Derivatives of Group IVB Elements-----	169
D. The Attempted Preparation of Pseudohalogen Derivatives of Silylmethane-----	176
IV. Summary-----	180
V. Appendix; Symbols and Abbreviations-----	182
VI. Bibliography-----	183

INDEX TO TABLES

	<u>Page</u>
I. Introduction	
1	3
2	4
3	5
4	9
5	9
6	10
7	18
8	20
9	21
II. Experimental	
1	31
2	33
3	43
4	43
5	45
6	47
7	47
8	50
9	54
10	55

INDEX TO TABLES

	<u>Page</u>
II. Experimental (Cont.)	
11 Retention Times for the G. C. Separation of (GeH ₃) ₂ CHCH ₃ from Impurities-----	56
12 Precise Mass Measurement Data for (GeH ₃) ₂ CHCH ₃ -----	57
13 Observed Fragmentation Pattern for (GeH ₃) ₂ CHCH ₃ -----	61
14 Group Mass Peak Assignments for (GeH ₃) ₂ CHCH ₃ -----	62
15 Retention Times for the G. C. Separation of CH ₂ =CHCH ₂ GeH ₃ from Impurities-----	63
16 Vapor Pressure of 3-Germylpropene-----	64
17 Data for CH ₂ =CHCH ₂ GeH ₃ Derived from Vapor Pressure Plot-----	66
18 Infrared Absorption Frequencies of CH ₂ =CHCH ₂ GeH ₃ ----	68
19 Observed Fragmentation Pattern for CH ₂ =CHCH ₂ GeH ₃ ----	70
20 Group Mass Peak Assignments for CH ₂ =CHCH ₂ GeH ₃ -----	71
21 Retention Times for the G. C. Separation of GeH ₃ CH ₂ SCH ₃ from Impurities-----	72
22 Infrared Absorption Frequencies of GeH ₃ CH ₂ SCH ₃ -----	75
23 Proton Magnetic Resonance Data for GeH ₃ CH ₂ SCH ₃ -----	76
24 Observed Fragmentation Pattern for GeH ₃ CH ₂ SCH ₃ -----	78
25 Group Mass Peak Assignments for GeH ₃ CH ₂ SCH ₃ -----	79
26 Retention Times for the G. C. Separation of CH ₂ =CHCH ₂ SiH ₂ F and CH ₂ =CHCH ₂ SiHF ₂ from Impurities--	84
27 Precise Mass Measurement Data for Mono- and Difluorosilylpropene-----	85
28 Vapor Pressure of 3-Monofluorosilylpropene-----	86
29 Data for CH ₂ =CHCH ₂ SiH ₂ F Derived from Vapor Pressure Plot-----	88
30 Infrared Absorption Frequencies of CH ₂ =CHCH ₂ SiH ₂ F--	91
31 Infrared Absorption Frequencies of CH ₂ =CHCH ₂ SiHF ₂ --	92

INDEX TO TABLES

	<u>Page</u>
II. Experimental (Cont.)	
32	Mass Spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ ----- 93
33	Vapor Pressure of 1,1'-Difluorotrisilylamine----- 98
34	Data for $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$ Derived from Vapor Pressure Plot----- 98
35	Infrared Absorption Frequencies of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$ --- 101
36	Precise Mass Measurement Data for Fluorotrisilyl- amines----- 102
37	Proton Magnetic Resonance Data for Fluorotrisilyl- amines----- 103
38	Mass Spectrum of $(\text{SiH}_3)_2\text{NSiH}_2\text{F}$ ----- 105
39	Mass Spectrum of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$ ----- 106
40	Mass Spectrum of $(\text{SiH}_2\text{F})_3\text{N}$ ----- 107
41	Proton Magnetic Resonance Data for $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$ and $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$ ----- 132
42	Proton Magnetic Resonance Data for $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ -- 133
43	Fluorine-Hydrogen Coupling Constants for $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ ----- 134
III. Discussion	
1	Certain Frequencies Used in Assigning <u>Trans</u> and <u>Gauche</u> Forms of 1,2-Digermylethane----- 143
2	Comparison of Selected Absorption Frequencies of Various Organogermenes----- 144
3	Proton Magnetic Resonance Data for Selected Alkyl- germanes----- 145
4	Proton Magnetic Resonance Data for Germylmethyl Methyl Sulfide and Some Related Compounds----- 146
5	Mass Spectral Data for Some Digermyl Organic Derivatives----- 147

INDEX TO TABLES

	<u>Page</u>
III. Discussion (Cont.)	
6 Comparison of Selected Absorption Frequencies for Silylpropenes and Some Related Compounds-----	156
7 Proton Magnetic Resonance Data for Fluorinated Trisilylamines and Some Related Compounds-----	167
8 Proton Magnetic Resonance Data for Several Substituted Propenes-----	174
9 Syntheses of Some Pseudohalogen Derivatives of Silane and Organosilanes-----	177
10 Structural Studies on Some Pseudohalogen Derivatives of Silane-----	178

INDEX TO FIGURES

	<u>Page</u>
I. Introduction	
A Conformations of Analogous Carbon, Silicon and Germanium Derivatives-----	7
II. Experimental	
A Vacuum Apparatus for Reactions Using Liquid Ammonia or HMPT as Solvent-----	25
B Low-Pressure Fractionating Column-----	27
C Inlet and Collection Systems for the Gas Chromatograph-----	28
D Collection Trap for the Gas Chromatograph-----	30
E Vapor Pressure of $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ -----	46
F Infrared Spectrum of $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ -----	49
G CH_2 Proton Resonance at 50 Hz. Sweep Width (for $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$)-----	51
H GeH_3 Proton Resonance at 50Hz. Sweep Width (for $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$)-----	52
I Infrared Spectrum of $(\text{GeH}_3)_2\text{CHCH}_3$ -----	58
J Vapor Pressure of $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$ -----	65
K Infrared Spectrum of $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$ -----	67
L Proton Magnetic Resonance Spectrum of $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$ at 600 Hz. Sweep Width (60 MHz.)-----	69
M Infrared Spectrum of $\text{GeH}_3\text{CH}_2\text{SCH}_3$ -----	74
N Proton Magnetic Resonance Spectrum of $\text{GeH}_3\text{CH}_2\text{SCH}_3$ plus $\text{ClCH}_2\text{SCH}_3$ Impurity (250 MHz.)-----	77
O Vapor Pressure of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ -----	87
P Infrared Spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ -----	89
Q Infrared Spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$ -----	90
R Proton Magnetic Resonance Spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ at 600 Hz. Sweep Width (60 MHz.)-----	94

INDEX TO FIGURES

	<u>Page</u>
II. Experimental (Cont.)	
S	Proton Magnetic Resonance Spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ at 1500 Hz. Sweep Width (250 MHz.)----- 95
T	Vapor Pressure of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$ ----- 99
U	Infrared Spectrum of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$ ----- 100
V	Proton Magnetic Resonance Spectra of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$ and $(\text{SiH}_2\text{F})_3\text{N}$ at 250 Hz. Sweep Width (100 MHz.)---- 104
W	Proton Magnetic Resonance Spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$ at 600 Hz. Sweep Width (60 MHz.)----- 117
X	Experimental and Calculated Proton Magnetic Resonance Spectra of $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$ (100 MHz.; -CH ₂ - and CH ₂ = Resonances)----- 118
Y	Proton Magnetic Resonance Spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$ at 300 Hz. Sweep Width (250 MHz.; -CH ₂ - and CH ₂ = Resonances)----- 119
Z	-CH ₂ - Proton Resonance at 90 Hz. Sweep Width (250 MHz.; for $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$)----- 120
AA	CH ₂ = Proton Resonance at 90 Hz. Sweep Width (250 MHz.; for $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$)----- 122
BB	Experimental and Calculated Proton Magnetic Resonance Spectra of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ (100 MHz.; -CH ₂ -, CH ₂ = and SiH ₂ Resonances)----- 123
CC	Experimental and Calculated Proton Magnetic Resonance Spectra of $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$ (100 MHz.; -CH ₂ - and CH ₂ = Resonances)----- 124
DD	=CH- Proton Resonance at 30 Hz. Sweep Width (60 MHz.; for $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$)----- 125
EE	=CH- Proton Resonance at 30 Hz. Sweep Width (250 MHz.; for $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$)----- 126
FF	Calculated Proton Magnetic Resonance of $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$ (=CH- Resonance)----- 128
GG	Calculated Proton Magnetic Resonance of $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$ (=CH- Resonance) Ignoring SiH ₃ Splitting----- 129

INDEX TO FIGURES

	<u>Page</u>
III. Discussion	
A The Progress of the Reaction of PF_5 and $(\text{SiH}_3)_3\text{N}$	162,
as Observed by Proton Magnetic Resonance-----	163

ABSTRACT

In the present research project, the synthetic utility of alkali metal derivatives of germane has been explored. 1,2-Digermylethane has been prepared by the reaction of solid sodium germyl with 1,2-dichloroethane. The compound is an analogue of butane and has been characterized by its infrared, mass and proton magnetic resonance spectra, as well as by other means.

1,1-Digermylethane and 3-germylpropene have been synthesized in a similar manner by the reaction of the corresponding chloro compound with solid sodium germyl. Although only trace amounts of 1,1-digermylethane were obtained, it was possible to record its infrared, mass and proton magnetic resonance spectra. The previously reported compound 3-germylpropene was characterized in this work by its infrared, mass and proton magnetic resonance spectra, as well as by other means.

The synthesis of germylmethyl methyl sulfide has been accomplished by the reaction of chloromethyl methyl sulfide with potassium germyl in hexamethylphosphortriamide (HMPT). The new sulfide prepared is unstable at room temperature, although its infrared, mass and proton resonance spectra could be obtained.

The selective fluorination of the Si-H bond(s) of allylsilane and certain silyl ethers and amines by phosphorus pentafluoride has been investigated. The new compounds 3-monofluorosilylpropene, 1-monofluoro-, 1,1'-difluoro- and 1,1',1''-trifluorotrisilylamine were prepared by this method. In addition, the previously known compound 3-difluorosilylpropene was prepared by this route. 3-Monofluorosilylpropene and

1,1'-difluorotrisilylamine were characterized by infrared, mass and proton resonance spectra, as well as by other means. The remaining compounds were characterized as fully as their quantities permitted.

The high resolution proton magnetic resonance spectra of the compounds 3-silylpropene, 3-monofluorosilylpropene and 3-germylpropene were analyzed by using the computer program LAOCN 3. The results of the analysis were used to investigate the possible interaction between the unoccupied d orbitals of the group IVB element and the olefinic $p\pi$ orbitals. There was no indication for the presence of any inter- or intramolecular interaction of this type. The molecules apparently exist almost entirely in the gauche conformation.

INTRODUCTION

A. Present Research

The study of hydrides and hydride derivatives of the lower group IVB elements has led to significant contributions to fundamental research in inorganic chemistry. Until recently, most of the work in this field dealt with the preparation and characterization of the silicon hydrides (silanes) and silane derivatives. Credit and admiration must be extended to Alfred Stock who, in the days before spectroscopic and other modern analytical techniques, synthesized and determined the properties of many silanes and some of their simple derivatives. Since then, a large number of silanes and silane derivatives have been prepared. Excellent discussions of these compounds have been given in several review articles by Aylett,⁹ Ebsworth,⁵⁸ MacDiarmid,^{125, 127, 128} Mackay¹²⁹ and Van Dyke.¹⁹³ These references should be consulted for further background information. Silanes have been utilized more than any other group of hydrides for testing bonding theories owing to the wider range of compounds known. Silicon hydride molecules are usually small and uncomplicated, thus allowing convenient examination by physical techniques. They are also often very volatile under low pressure and thus easily manipulatable in a vacuum line.

Until recently, only a small number of germanium hydrides (germanes) and their derivatives had been prepared and characterized. At one time, this appeared to be due to their instability and to difficulties in synthetic procedures. Lately, however, preparations of the parent germanes and their derivatives have been more successful and there are excellent reviews on the subject by Jolly and Norman¹¹⁰ and Van Dyke.¹⁹⁴

In an attempt to increase the list of synthesized and characterized germanes, it was undertaken as part of the present research to investigate the synthetic potential of reactions between alkali metal derivatives of germane and organohalides using hexamethylphosphortri- amide (HMPT) and liquid ammonia as solvents. The work resulted in the preparation of three new compounds, two of which, however, were not thermally stable, and in a new route to a previously known compound.

A second research project undertaken involved an investigation concerning the synthetic possibilities of selective fluorination of (1) organosilanes, (2) organosiloxanes and (3) silylamines. Five new compounds resulted from this project, two of which were well characterized. The new fluorosilylamines offer opportunities for future interesting bond angle studies and other bonding considerations.

Finally, high resolution proton magnetic resonance studies were performed on three allyl derivatives of silane and germane (i.e., 3-substituted propenes). It was hoped that these studies would yield information about the molecular conformations of the compounds and possibly some evidence for inter- or intramolecular bonding involving the unsaturated linkage and the d orbitals of silicon or germanium.

B. General Aspects of Group IVB Elements and Their Compounds

Some basic properties of the group IVB elements are reviewed in this section. Many of these will be used later in discussing the results obtained in the present research project.

1. Properties of the Group IVB Elements

Several of the basic properties of the group IVB elements are summarized in Table I-1.

Table I-1
Some Basic Properties of the Group IVB Elements¹⁵⁰

Element	Atomic Number	Atomic Weight	Covalent Radius (Å)	Element-Carbon Bond Length (Å) ^a
C	6	12.01	0.77	1.54
Si	14	28.09	1.17	1.94
Ge	32	72.59	1.22	1.99
Sn	50	118.69	1.40	2.17
Pb	82	207.19	1.52	2.29

^a For tetraalkyl compounds

Most of the data do not need to be discussed at this point, although it is of interest to note that an unexpectedly small change occurs in the covalent radius from silicon to germanium. An explanation for this is the so-called "lanthanide contraction", resulting from the occurrence of the first transition series between the two elements. The observed small increase in covalent radius coupled with an increase in atomic number of 18 results in a greater electron-density for germanium than would be expected and most likely influences the relative electronegativities of silicon and germanium. The increasing covalent radius of the group IVB elements also diminishes the stability of the element-carbon bond, for there is a decrease in bond energy expected due to the larger interatomic distances.

2. Electronic Configuration

The arrangement of electrons around a group IVB atom influences its chemical reactivity. The electronic configurations of group IVB elements are listed in Table I-2.

Table I-2

Electronic Configuration of Group IVB Elements in the Ground State¹⁵⁰

Principle shell number Element	n=1 s	n=2 s p	n=3 s p d	n=4 s p d f	n=5 s p d f	n=6 s p
C	2	2 2				
Si	2	2 6	2 2			
Ge	2	2 6	2 6 10	2 2		
Sn	2	2 6	2 6 10	2 6 10	2 2	
Pb	2	2 6	2 6 10	2 6 10 14	2 6 10	2 2

It is noted that all group IVB elements have four valence electrons in their ground states, i.e. (ns^2np^2). There is a tendency to form four covalent bonds by the promotion of an s electron into an empty p orbital: ($ns^2np^2 \rightarrow ns^1np^3$), followed by the well-known sp^3 orbital hybridization.

All group IVB elements, except for carbon, have vacant low-lying d orbitals which are potentially available for bonding. The ability of the elements below carbon to increase their coordination numbers to values greater than four most likely is related to this availability of d orbitals.^a The hybridization between one or two of these d orbitals and available s or p orbitals has been used to explain five- and six-coordinated molecules, respectively, containing a lower group IVB element.^{48,184} Some examples of these molecules are $SiCl_4 \cdot N(CH_3)_3$ (sp^3d), $SiHF_3 \cdot N(CH_3)_3$ (sp^3d), SiF_6^{2-} (sp^3d^2) and $SiCl_4 \cdot 2py$ (sp^3d^2). Such coordination by a nucleophilic

^a Carbon presumably might increase its coordination number to five or six by hybridizing with unoccupied orbitals, but the lowest orbitals available are in the next highest shell.² The large promotional energies required to effect hybridization with these higher orbitals lead us to assume that such participation is minimal for carbon.

reagent, e.g., OH^- or NH_2^- , has also been proposed as an important step in the substitution of silanes and Eaborn has suggested a lowering of the activation energy by a coordination of this type.⁵⁶

3. Electronegativity

Pauling originally defined electronegativity as "the power of an atom in a molecule to attract electrons to itself."¹⁴³ Other definitions have since followed, most of which are still somewhat related to Pauling's. Pauling's electronegativity list for the group IVB elements (see Table I-3) has carbon as the most electronegative, while the remaining members of the series are about equivalent but less electronegative than carbon.

Table I-3
Various Electronegativity Assignments to the Group IVB Elements

	C	Si	Ge	Sn	Pb
Pauling ¹⁴³	2.5	1.8	1.8	1.8	1.8
Allred ^{a,1}	2.55	1.90	2.01	1.96	2.33
Gordy ⁸⁵	2.52	1.82	1.77	1.61	1.56
Huggins ¹⁰⁰	2.60	1.90	1.90	1.90	--
Pritchard and Skinner ¹⁴⁶	2.51	1.84	1.87	1.73	--
Sanderson (Stability Ratios) ^{165,166}	2.47	1.74	2.31	2.03	2.37
Allred and Rochow ²	2.60	1.90	2.00	1.93	2.45

^a Calculated by Pauling's method using more recent thermochemical data.

Of the subsequent authors proposing electronegativity scales, some have agreed with these assignments^{85,100,146} and some have not.^{1,2,165,166} Electronegativity scales proposed by the latter group indicate that germanium is more electronegative than silicon or tin.

There are two main problems in assigning an absolute electronegativity scale; first, electronegativity is impossible to measure directly, for there are other factors involved which would have an effect on the measurement, and second; the electronegativity is most likely not a constant, but would depend on the groups bound to the element and on other perturbations such as hybridization. As a result, one should consider electronegativity as a qualitative concept, realize that reliance should be placed only on large differences, and accept the values of silicon, germanium and tin (and possibly lead) as approximately equal.

The polarizability of the elements has been suggested as more important in determining reactivity differences and most likely increases with atomic size as one descends group IVB.¹⁵⁰

4. Properties Explained by the Existence of $(p \rightarrow d)\pi$ Bonding

The concept of $(p \rightarrow d)\pi$ bonding has been invoked by many workers to account for the differences found on comparing certain properties of analogous compounds of carbon, silicon and germanium. Theoretical arguments supporting this π -interaction were first discussed in some detail by Jaffe¹⁰² and Craig, et al.⁴⁸ Among the properties are: (a) bond angles, (b) bond lengths, (c) bond energies, (d) Lewis basicities and (e) photo-electron spectra.

a. Bond Angles

Some of the variations in bond angle between carbon, silicon and germanium compounds are shown in Figure I-A. The methods of determining the angle are enclosed in parentheses beneath the conformation; references are in parentheses to the right of the conformation.

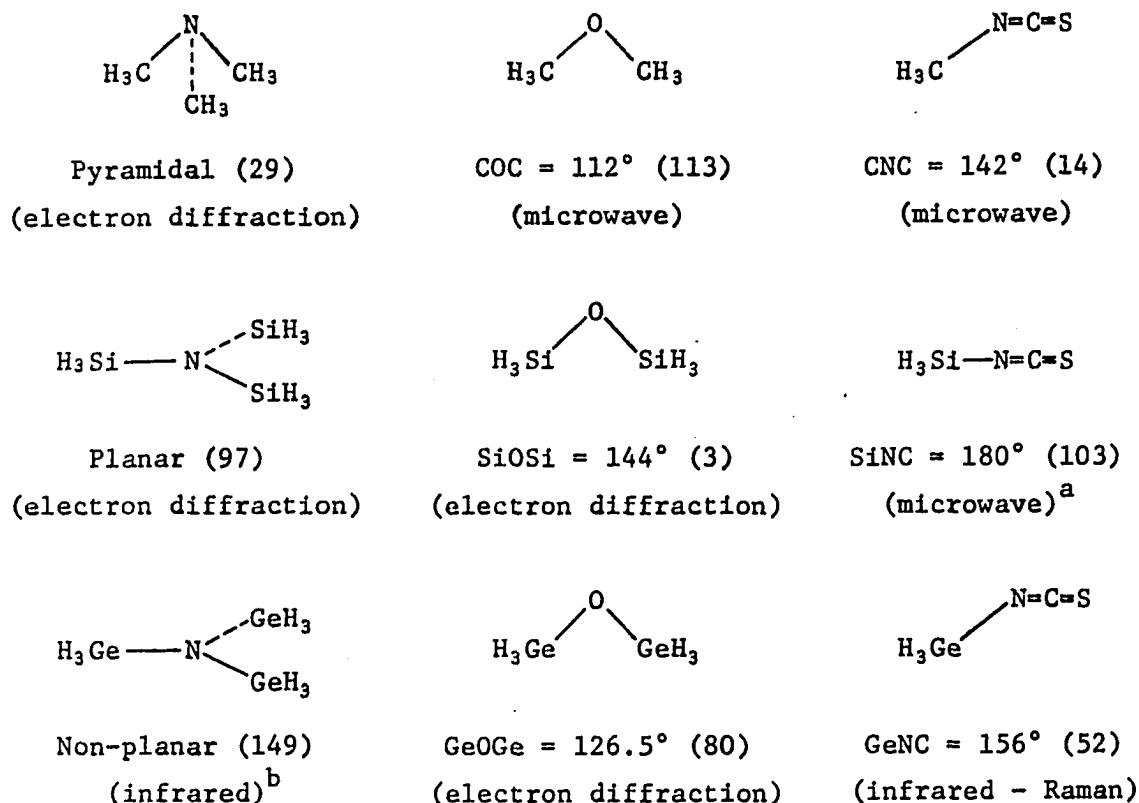


Figure I-A -- Conformations of Analogous Carbon, Silicon and Germanium Derivatives^{9,194}

^a An SiNC angle of 159° has recently been reported for SiH_3NCS determined by electron diffraction.¹⁷² The inconsistency may be due to the excitation of a low-frequency skeletal bending mode which affects the electron diffraction determination.

^b The conformation of $(\text{GeH}_3)_3\text{N}$ has been reinvestigated by electron diffraction and results indicate a planar structure.⁷⁹

The increase in bond angle from carbon to silicon has been accounted for by overlap of the lone-pair p orbital (or orbitals) on nitrogen or oxygen with vacant d orbitals on silicon. It has been suggested that the shape changes so that the p character of lone-pair orbitals increases and therefore greater overlap can occur.⁹

The structural parameters for germanium analogues have led to the opinion that p-d overlap occurs in these compounds, but to a lesser extent than in silicon compounds. Reasons given for this difference in (p → d)π bonding have been the difference in electron density of the orbitals (silicon's 3d orbitals would be less diffuse than germanium's 4d orbitals) or perhaps the presence of a radial node in germanium's d orbitals but not in silicon's.¹⁹¹

b. Bond Lengths

In 1934, it was noticed the bond lengths in silicon tetrahalides were much shorter than would be expected from covalent radii.³⁰ It was to explain these abnormally short bond lengths that partial double-bonding involving silicon d orbitals was first proposed. The differences in bond lengths between predicted and experimental may be seen in Table I-4.

c. Bond Energies

Table I-5 shows that silicon-element bond energies are 30-40% greater than predicted.^{129,136} It is generally proposed that this is a result of Si-X bonds (X = N, O, halogen) with an effective bond order greater than one, i.e. (p → d)π bonding.

d. Lewis Basicity

The Lewis basicities of ethers and amines are well known. If a silyl group is substituted for a methyl group in various amines and

Table I-4
Bond Lengths for Various Silyl Compounds⁹

Bond	Sum of Covalent Radii (Å)	"Corrected" Sum ^a (Å)	Exptl. Bond Length (Å)	Compound	Ref.
Si-N	1.87	1.76	1.73	(SiH ₃) ₃ N	97
			1.71	SiH ₃ NCS	103
Si-O	1.83	1.68	1.63	[(CH ₃) ₃ Si] ₂ O	210
			1.63	(SiH ₃) ₂ O	3
Si-F	1.81	1.61	1.54	SiF ₄	30
			1.59	SiH ₃ F	12

^a Corrected by the Schomaker-Stevenson equation to account for changes due to the ionic character of the Si-X bond.

Table I-5
Energies of Various Carbon and Silicon Bonds⁹

	H	F	Cl	Br	I	N	O
C ^a	99	116	78	68	51	73	86
Si (experimental) ^a	76	135	91	74	56	85 ^c	108
Si (predicted) ^b	76	89	60	52	39	56	66
$\frac{\text{Si (exptl.)} - \text{Si (predicted)}}{\text{Si (exptl.)}} \times 100$	0	34	30	30	30	34	39

^a Reference 43

^b Reference 129, 136

^c Estimated

ethers, one would expect, due to the lower electronegativity of silicon, an increase in the availability of the lone-pair p electrons on oxygen and nitrogen, and thus an increase in Lewis basicity.

When this substitution is effected, however, a decrease in Lewis basicity occurs, as indicated by the data in Table I-6. The observed lower base strengths of silicon ethers relative to carbon ethers have been accounted for by p-d overlap. The lone-pairs of electrons on an oxygen attached to silicon are apparently delocalized onto the latter's d orbitals and therefore are not as available for donation to a reference Lewis acid as would be expected without the delocalization. Similar results are obtained in the case of amines.^{10,32,185}

Table I-6
Relative Lewis Basicities of Various Ethers

Base	$\Delta\nu^a$ (cm ⁻¹)	Reference
CH ₃ OCH ₃	128	200
C ₂ H ₅ OC ₂ H ₅	144	192
CH ₃ OSiH ₃	92	200
CH ₃ OSiH ₂ CH ₃	114	200
SiH ₃ OSiH ₃	0	192
CH ₃ OGeH ₃	153	76

^a $\Delta\nu$ is the difference in frequency between free OH and hydrogen-bonded OH. With a given reference acid, $\Delta\nu$ is known to be greater for the stronger Lewis base. The above $\Delta\nu$ values are obtained using methanol as the reference Lewis acid.

Germyl ethers, however, show the expected increase in Lewis basicity. This is in agreement with the previously discussed conclusions from structural studies that $(p \rightarrow d)\pi$ bonding occurs less extensively in Ge-O than in Si-O linkages.

e. Photo-electron Spectra

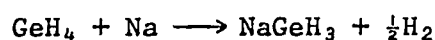
The photo-electron spectra of silyl and germyl halides provide the latest evidence for $(p \rightarrow d)\pi$ bonding.⁴⁴ In a photo-electron spectrum, an electron excited from a nonbonding orbital displays an intense vibrationless band which often precedes bands of low intensity. The latter bands seem to be due to the formation of ions possessing some amount of vibrational energy. Excitation from bonding or antibonding orbitals, however, yield broad spectra because the electrons are being excited to various vibrational levels of the molecular ion.

The compounds examined by this technique, i.e. methyl, silyl, and germyl halides, have given spectra which contain greater band widths for the silyl and germyl compounds than for the corresponding methyl compound. (Exceptions are the fluorides which yield broad bands with smooth contours for all.) The electrons excited are the lone-pairs on the halogens. The most notable differences were observed in connection with the chlorides. CH_3Cl has a nonbonding band contour, while the shapes of the SiH_3Cl and GeH_3Cl bands closely resemble those expected for excitation of a bonding or antibonding electron. It would therefore seem likely that the lone-pairs of electrons on chlorine overlap with the unoccupied d orbitals of the central element, acquiring some partial bonding character.

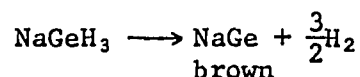
C. Background Information Concerning Reactions Investigated in the Present Research Project

1. Synthesis of Alkali Metal Derivatives of Germane

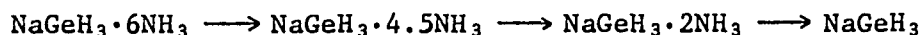
The first alkali metal derivative of a lower group IVB hydride was prepared by Kraus and Carney in 1934.¹¹⁹ By bubbling germane through a solution of sodium in liquid ammonia, they obtained a product which was called "sodium trihydrogermanide", i.e. NaGeH₃. The proposed reaction was written



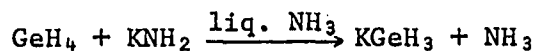
Upon removal of ammonia, a white solid was obtained which decomposed to a brown color after several hours at room temperature and which reacted readily with oxygen. The suggested thermal decomposition reaction was



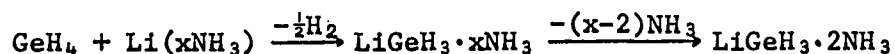
It was also determined in this early study that NaGeH₃ crystallizes from liquid ammonia as NaGeH₃·6NH₃. The ammonia of crystallization is then removed in several stages



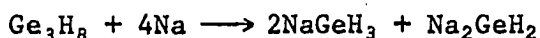
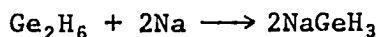
Sixteen years later, Teal and Kraus prepared the analogous potassium salt, KGeH₃, by the same method and found it to have properties similar to those of the sodium derivative, though it was somewhat more stable.¹⁸⁸ KGeH₃ may also be prepared by reaction of germane with potassium amide⁷⁸



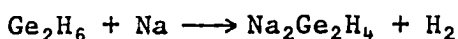
Recently, Amberger and Boeters have reported the preparation of LiGeH₃ by the reaction of germane with lithium in liquid ammonia.⁴ A pale gray solid remained after removal of the excess ammonia and was identified as LiGeH₃·2NH₃



The interaction of digermane and trigermane with sodium in liquid ammonia has been studied conductometrically by Emeleus and Mackay.⁶⁷ The results indicate an essentially complete cleavage of Ge-Ge bonds with the formation of the sodium derivative:

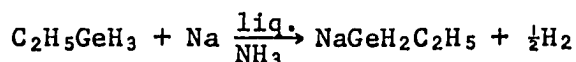


Hydrogen evolution studies of the systems, however, suggest that other reactions, such as

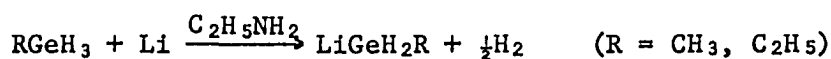


also occur.⁶⁷ Alkali metal derivatives of the higher germanes have not yet been isolated or characterized.

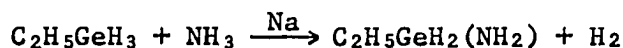
These reactions in liquid ammonia were further extended to alkyl germanes by Glarum and Kraus, as illustrated by the following reaction:⁷⁸



Other ammonia type solvents have been investigated in the synthesis of this type of compound. For example, Glarum and Kraus have prepared the lithium derivative by the reaction of lithium with an alkyl germane in ethylamine⁷⁸



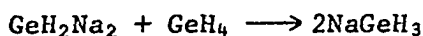
In the reaction of ethylgermane with sodium, the authors discovered that an excess of ethylgermane was required to complete the reaction and that an excess of hydrogen gas was evolved.⁷⁸ A side reaction was proposed, proceeding according to the equation



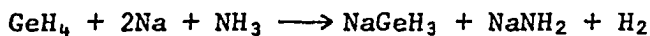
At one time it was thought that the reaction of germane with sodium in liquid ammonia initially proceeded by the reaction⁶⁷



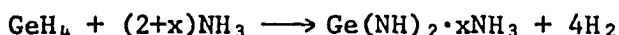
The Na_2GeH_2 would then react further to form NaGeH_3



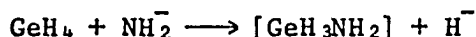
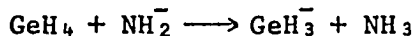
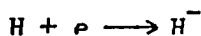
However, it was later shown by Rustad and Jolly that the reaction actually proceeded according to the following general equations¹⁶¹



An excess of GeH_4 is necessary to completely convert the sodamide to the germyl derivative. The evolution of excess hydrogen found by Glarum and Kraus may be explained by a side reaction of the type



The formation of this germanium imide and the previously mentioned sodamide can be accounted for by the following proposed mechanism¹⁶¹



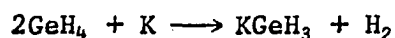
The $[\text{GeH}_3\text{NH}_2]$ intermediate probably reacts with ammonia to produce $\text{Ge}(\text{NH}_2)_4$ or $\text{Ge}(\text{NH})_2$.

Recently, several groups of workers have recognized the importance of these metal derivatives as intermediates for the synthesis of a wide variety of germyl and related compounds and have investigated other methods for their preparation. For example, Cradock, Gibbon and Van Dyke have studied the use of the aprotic solvent hexamethylphosphortriamide (HMPT) for the synthesis of alkali metal derivatives of silane and germane.⁴⁷ HMPT has very low volatility under reduced pressure and is moderately chemically inert. Dissolution of an alkali metal in HMPT produces a deep

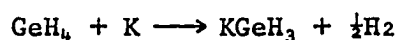
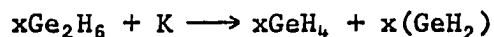
blue solution similar to that formed by alkali metal-liquid ammonia solutions. (Potassium seems to dissolve more rapidly than sodium.) Upon reaction with silane or germane, MSiH_3 or MGeH_3 ($\text{M} = \text{Na}, \text{K}$) is formed and the solution turns a pale yellow. The solid salts cannot be isolated due to the nonvolatile nature of the solvent. The metal salts were characterized by their reactions with a variety of alkyl halides (section C.4.).

Bornhorst and Ring have prepared potassium germyl by reacting excess germane with potassium in 1,2-dimethoxyethane (monoglyme) at -78° until the solution turned blue (2-40 hours).²² The solvent was removed by distillation until the salt was just free flowing and further reactions were performed with this material. Rustad and Jolly prepared the KGeH_3 using the same method, but did not remove any of the solvent before reacting the material with various compounds (section C.4.)^{123,162}

The interaction of a Na/K alloy (80:20 weight percent) with germane in monoglyme or bis(2-methoxyethyl) ether (diglyme) to yield KGeH_3 has been reported by Amberger and Mühlhofer.⁵ The reaction is reported to require 12 hours unless the hydrogen formed is removed after 15-20 minutes at room temperature:¹⁹⁴

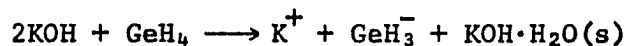


The reaction of potassium with digermane in monoglyme has been investigated by Garrity and Ring and is described by the following two equations:⁷⁵



Potassium germyl does not seem to form directly from digermane in this reaction.

One of the better preparations of the potassium salt is the deprotonation of germane with excess potassium hydroxide in solvents such as dimethyl sulfoxide or monoglyme.^{106,107,108} Excess KOH is used to dry the solvent and remove water formed in the reaction as the hydroxide hydrate. The net reaction may be written as



The germyl anion may then react with an alkyl halide to give an alkyl germane as in other solvents. Full details of the use of KGeH_3 prepared by this method are described by Rustad, Birchall and Jolly.¹⁶⁰

2. Synthesis of Alkali Metal Derivatives of Silane

In the 1930's, S. Isenberg observed a white crystalline material as the product of a rapid reaction of potassium metal with silane in liquid ammonia.¹⁰¹ The action of ammonium cations regenerated silane and addition of methyl chloride produced methylsilane. These properties made it obvious that KSiH_3 was present but ammonolysis prevented its isolation.

Ring and Ritter finally isolated cubic crystals of potassium silyl in 1960.¹⁵² KSiH_3 was prepared by condensing potassium (introduced by distillation), monoglyme and silane into a vessel and allowing them to react for one to two months. Removal of the solvent yielded the crystals.¹⁵² When potassium sand was used, the reaction was usually complete after 24-48 hours.¹¹⁴ Silane and a Na/K alloy in monoglyme produced KGeH_3 as well.¹⁵²

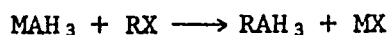
Potassium silyl has also been prepared by treating potassium hydride with excess disilane in monoglyme at room temperature for 24 hours.¹⁵²

3. Synthesis of Alkali Metal Derivatives of Stannane

Emeléus and Kettle⁶⁶ showed the existence of sodium stannyl and disodium stannylene (NaSnH₃ and Na₂SnH₂) by conductometric titration of a sodium-ammonia solution with stannane. Sodium stannyl is unstable but reacts in liquid ammonia with alkyl iodides to form alkyl stannanes.

4. Reactions of Alkali Metal Derivatives of the Lower Group IVB Hydrides

Most of the reactions of the alkali metal derivatives of the group IVB hydrides are of the coupling type, where the derivative is allowed to react with an organic or inorganic halide. The reaction may be written

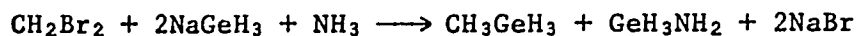


where M = alkali metal, A = Si, Ge, Sn, R = organic or inorganic group and X = halogen. Some of the reaction systems are summarized in Table I-7.

It is important to note that some deviations to the coupling reactions occur when C₆H₅Br or certain dihalo organic compounds are allowed to react with the alkali metal salts. The reaction of phenyl bromide with sodium germyl does not yield phenyl germane, but rather benzene, sodium bromide and the germane polymer:⁷⁷



Also, the reaction of methylene bromide with sodium germyl produces methylgermane, germyl amide and sodium bromide:



Dreyfus and Jolly conclude that the reaction between organohalides and MGeH₃ may proceed in two different ways:⁵³

(1) Nucleophilic attack by germyl anion on carbon

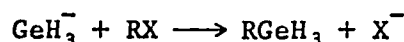
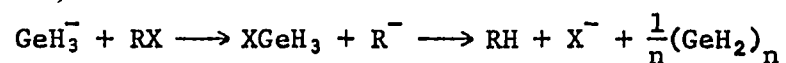


Table I-7
Reaction Systems of Alkali Metal Derivatives
of Silicon, Germanium and Tin Hydrides

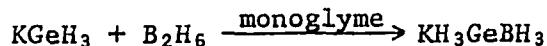
Alkali Metal Derivative	Halide	Solvent	Product	Reference
NaGeH ₃	CH ₃ I	liq. NH ₃	CH ₃ GeH ₃	188
KGeH ₃	CH ₃ I	HMPT	CH ₃ GeH ₃	47
KGeH ₃	CH ₃ I	monoglyme	CH ₃ GeH ₃	160
NaGeH ₃	C ₂ H ₅ Br	liq. NH ₃	C ₂ H ₅ GeH ₃	188
KGeH ₃	C ₂ H ₅ Br	HMPT	C ₂ H ₅ GeH ₃	47
NaGeH ₃	n-C ₃ H ₇ Br	liq. NH ₃	n-C ₃ H ₇ GeH ₃	188
NaGeH ₃	C ₅ H ₁₁ Br	liq. NH ₃	C ₅ H ₁₁ GeH ₃	78
NaGeH ₃	SiH ₃ Br	none	SiH ₃ GeH ₃	55
KSiH ₃	GeH ₃ Cl	monoglyme	SiH ₃ GeH ₃	114,199
NaGeH ₃	(CH ₃) ₃ SiCl	none	(CH ₃) ₃ SiGeH ₃	55
NaGeH ₃	SiH ₃ CH ₂ Cl	none	SiH ₃ CH ₂ GeH ₃	76
NaGeH ₃	(CH ₃) ₃ GeF	none	(CH ₃) ₃ GeGeH ₃	55
KGeH ₃	CH ₃ OCH ₂ Cl	HMPT	CH ₃ OCH ₂ GeH ₃	47
NaGeH ₃	CH ₃ OCH ₂ Cl	none	CH ₃ OCH ₂ GeH ₃	77
NaSnH ₃	CH ₃ I	liq. NH ₃	CH ₃ SnH ₃	66
NaSnH ₃	C ₂ H ₅ I	liq. NH ₃	C ₂ H ₅ SnH ₃	66
NaSnH ₃	n-C ₃ H ₇ I	liq. NH ₃	n-C ₃ H ₇ SnH ₃	66

(2) Nucleophilic attack by germyl anion on halogen

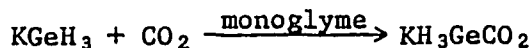


Reaction (2) is the major reaction when GeH₃⁻ replaces halide ion slowly.

Some other interesting reactions of KGeH_3 have been investigated by Jolly. In the reaction of potassium germyl with diborane, KH_3GeBH_3 is produced, which is the analogue of KBH_4 with one hydrogen replaced by a germyl group:¹⁶²



Also, the reaction of carbon dioxide with potassium germyl in monoglyme yields KGeH_3CO_2 which is presumed to be the structural analogue of potassium acetate:¹²³



5. Some Physical Properties of Alkali Metal Derivatives of Silane and Germane

Very little characterization of the alkali metal derivatives of the group IVB hydrides has been reported. In most cases, the compounds were characterized by preparation of the organic derivatives of the salt rather than the salt itself. However, there have been a few reports concerning the physical properties of the metal derivatives.

a. Crystal Structure of KSiH_3

Potassium silyl was studied by X-ray powder diffraction by Ring and Ritter.¹⁵¹ They found the structure to be cubic of the NaCl type, with the K positions at 000 , $\frac{1}{2}\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, the silicon positions at $00\frac{1}{2}$, $\frac{1}{2}00$, $0\frac{1}{2}0$, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and $a_0 = 7.15 \pm 0.02 \text{ \AA}$.

b. Proton Magnetic Resonance of Germyl Anions

Birchall and Jolly have obtained proton magnetic resonance of several germyl anions in ammonia.¹⁹ Some of the values are presented in Table I-8.

Table I-8
Proton Magnetic Resonance Data for Some Germyl Hydrides
and Their Anions¹⁹

Compound	$\delta_{\text{Ge-H}}^{\text{a}}$	$\delta_{\text{GeH-CH}_3}^{\text{a}}$	$\delta_{\text{GeH-C}_2\text{H}_5}^{\text{a}}$	$J_{\text{GeH-CH}}^{\text{b}}$	$J_{\text{GeH-C-CH}}^{\text{b}}$
GeH_4	2.98	--	--	--	--
GeH_4^-	0.99	--	--	--	--
CH_3GeH_3	3.22	0.19	--	4.22	--
$\text{CH}_3\text{GeH}_2^-$	2.19	-0.23	--	5.73	--
$(\text{CH}_3)_2\text{GeH}_2$	3.43	0.12	--	3.82	--
$(\text{CH}_3)_2\text{GeH}^-$	2.98	-0.16	--	4.90	--
$\text{C}_2\text{H}_5\text{GeH}_3$	3.26	--	0.93	2.8	0.5
$\text{C}_2\text{H}_5\text{GeH}_2^-$	2.33	--	1.16, 1.13, 1.07, 0.90	4.20	0.0
$(\text{C}_2\text{H}_5)_2\text{GeH}_2$	3.47	--	0.95, 0.89	2.73	0.5
$(\text{C}_2\text{H}_5)_2\text{GeH}^-$	3.10	--	1.02, 0.91 0.80	3.85	0.0

^a Values reported in ppm from external TMS.

^b Values reported in Hz.

A hydrogen removed from a parent hydride to give the anion results in shielding of the remaining protons and the chemical shift moves to higher field. The effect of substituting a methyl group for hydrogen causes deshielding of the remaining hydrogens, and the shift is to lower field. An ethyl group substitution causes a slightly greater deshielding than methyl and thus the ethylgermyl derivatives are slightly downfield from the corresponding methylgermyl derivatives.

c. Raman Spectra of the Germyl Anion

Recently, the Raman spectra of the germyl anion were obtained from solutions of $KGeH_3$ in liquid ammonia and monoglyme.¹⁸ The data reported are presented in Table I-9.

Table I-9

Raman Spectral Data for the Germyl Anion in Liquid Ammonia and Monoglyme¹⁸

Vibration	Ammonia ^a	Monoglyme ^a
ν_1	1739 \pm 6	1744 \pm 8
ν_2	814.5 \pm 1.5	839 \pm 9

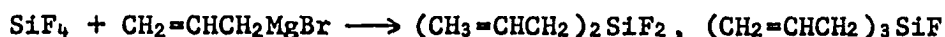
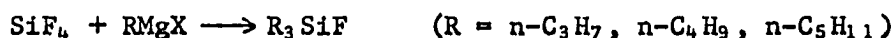
^a Frequencies are in cm^{-1} .

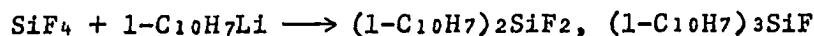
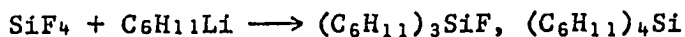
The data are consistent with a C_{3v} pyramidal structure. The vibrations ν_1 and ν_2 are the symmetric stretch and the symmetric bend vibrations respectively. The asymmetric bands were not observed.

6. Synthesis of Fluorosilanes

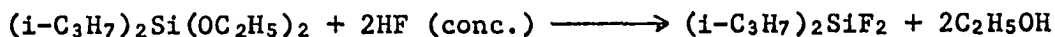
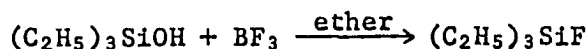
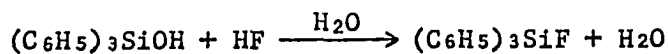
Although many fluorinated organosilanes have been reported in the literature, it has only been recently that organofluorosilanes containing silicon-hydrogen bonds have been investigated in any systematic way. As a general review, some common methods for the preparation of organofluorosilanes are summarized (with examples) below. A guide to the original literature references is given by Eaborn⁵⁶ and Van Dyke.¹⁹⁵

a. From SiF_4 and a Grignard reagent or organolithium reagent:

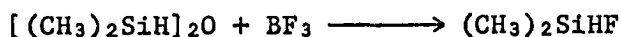
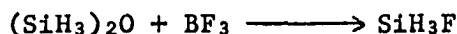
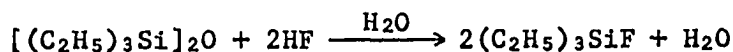
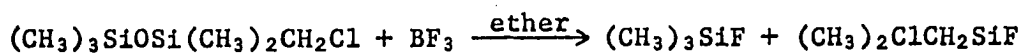




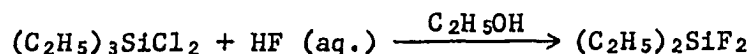
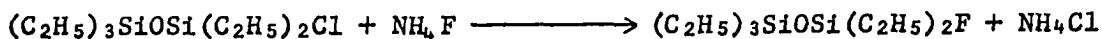
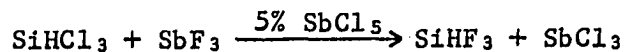
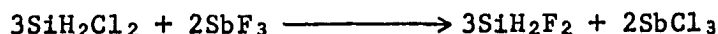
- b. From organosilicon alkoxides and hydroxides with boron trifluoride or hydrogen fluoride:



- c. From Lewis acid cleavage of siloxanes:

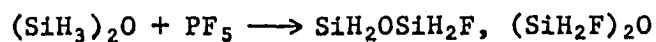


- d. From metal fluorides, ammonium fluoride or hydrogen fluoride with silicon halides:



In all of the above cases, it can be noted that an intermediate silicon halide, siloxane or related compound is required before it can be converted into an organosilicon fluoride. Organosilicon intermediates are usually available commercially for this conversion, but many intermediates containing Si-H bonds are not. In these latter cases, the

intermediate is usually prepared from an appropriate organosilane, purified, and then converted to the corresponding organofluorosilicon hydride. The purification procedure is often very tedious. It would be much more convenient if the starting organosilicon hydride could be converted directly to the fluorosilane. Certain investigators have recognized this and have been partially successful. For example, Kifer and Van Dyke have shown that PF_5 partially fluorinates $(\text{SiH}_3)_2\text{O}$:¹¹⁶



As will be described later in this thesis, we have investigated the partial fluorination of allyl silane and certain other silicon hydrides by this method.

EXPERIMENTAL

A. Apparatus and Techniques

1. Vacuum Apparatus

Volatile compounds in this research were manipulated in a conventional Pyrex glass vacuum system. Stopcocks and ground glass joints lubricated with Apiezon N grease permitted evacuation to a "working vacuum" of 10-20 microns when used with a two stage mercury diffusion pump and a Duo-Seal mechanical pump. A liquid nitrogen cooled waste trap was used to protect the pump.

The vacuum line and its manipulations have been thoroughly discussed in several comprehensive publications.^{54,104,154,174} Only modifications and new equipment will be discussed here.

2. Vacuum Apparatus for Reactions Using Liquid Ammonia or Hexamethylphosphortriamide as Solvent

Reactions involving the use of liquid ammonia or hexamethylphosphortriamide (HMPT) as a solvent were carried out in a special vacuum line. A schematic diagram of this line may be seen in Figure II-A. Evacuation was accomplished with a two stage mercury diffusion pump and a Cenco Hi-Vac 2 mechanical pump.

3. Fractionation

Routine separation of products was accomplished by vacuum distillation, adhering generally to the standard techniques described elsewhere.¹⁰⁴

The notation to be used throughout this work is as follows: R.T. \longrightarrow -78° \longrightarrow -196°. This indicates that a trap containing a mixture of substances to be fractionated was allowed to warm to room temperature while open to a series of two traps maintained at -78° and -196°. In addition,

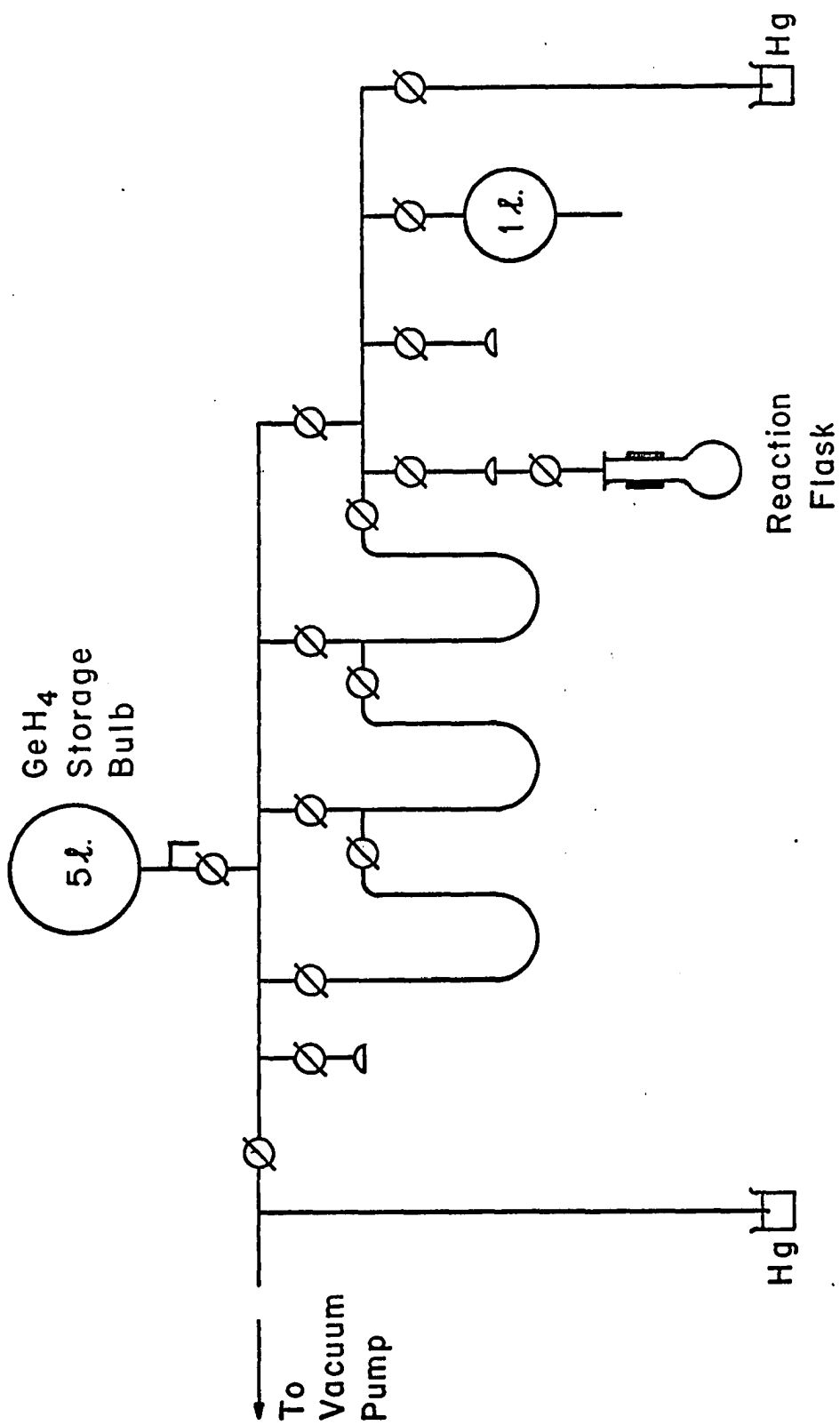


Figure II-A - Vacuum Apparatus for Reactions Using Liquid Ammonia or HMPT as Solvent

the substance of interest has condensed in the trap held at the underlined temperature. The separation is reasonably good if the substances to be separated differ in boiling points by 30°-40°. Whenever this condition was not met, one of the separation techniques discussed below was used.

A more agreeable separation was obtained with a low-pressure fractionating column¹⁰⁵ developed at Indiana University and modified in our laboratory by Mary Ann Finch (Figure II-B). Nitrogen gas, cooled by passing through a coil immersed in liquid nitrogen, was admitted at the top of the column. A temperature gradient of about 50° forms between the nitrogen inlet and outlet. The sample to be fractionated, held previously near the bottom at -196°, was allowed to expand onto the column and as the temperature was slowly increased, the sample refluxed up the column. The sample exit was monitored by an NRC model 721 vacuum gauge and each fraction directed to the appropriate collection trap as it came off the column. Substances with a boiling point difference of approximately 15° may be separated in this manner. The column was used only in the final stages of this research project.

The most efficient separation technique employed was gas chromatography. Nearly all of the compounds prepared in this research were fractionated by this method.

4. Gas Chromatography

The gas chromatographic separations in this research were accomplished on an Aerograph A 90-P3 instrument equipped with a thermistor bridge and a 4-way gas sampling valve.

A diagram of the Pyrex inlet and collection systems that were attached to the chromatograph may be seen in Figure II-C. Glass manifold

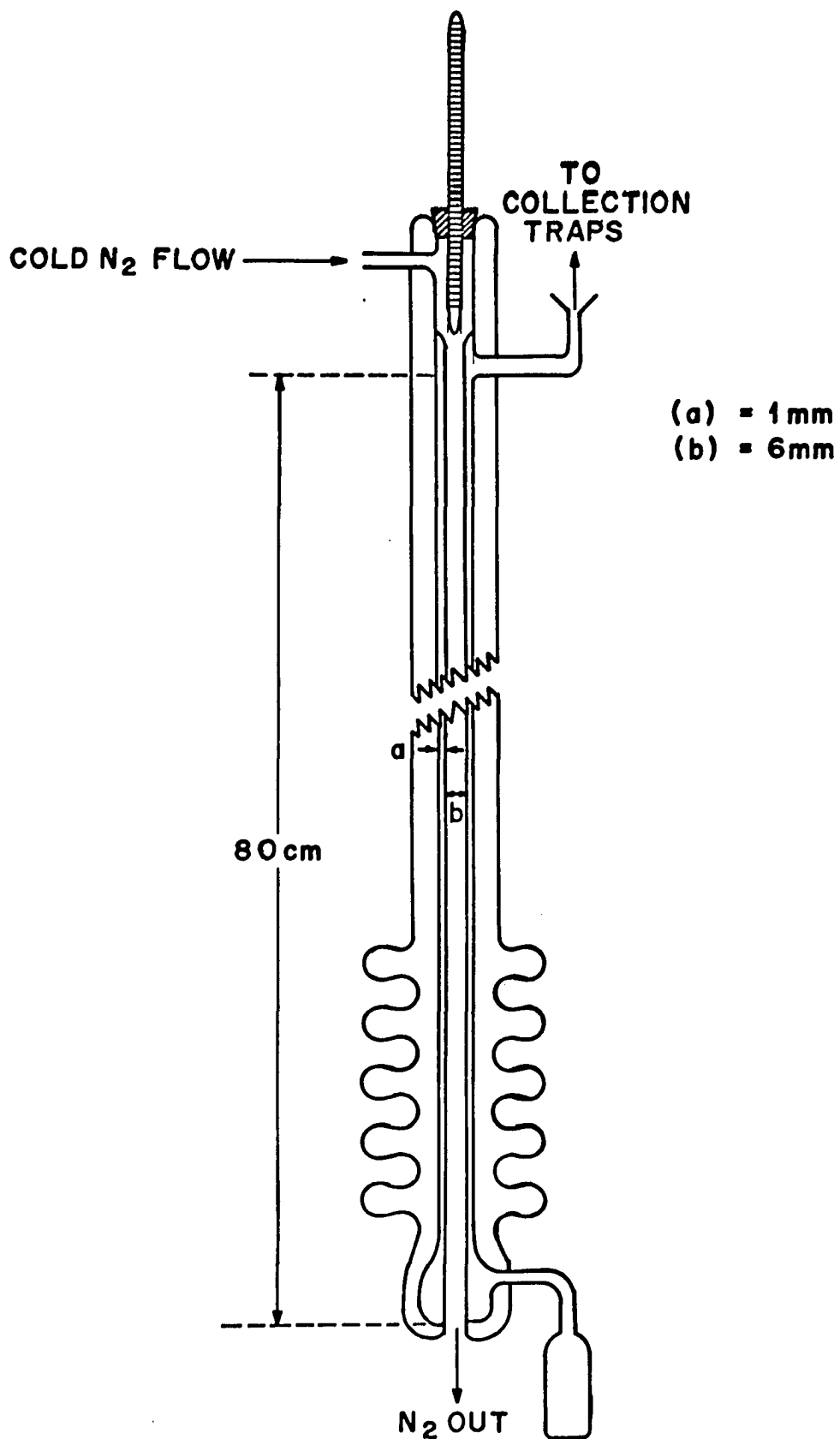
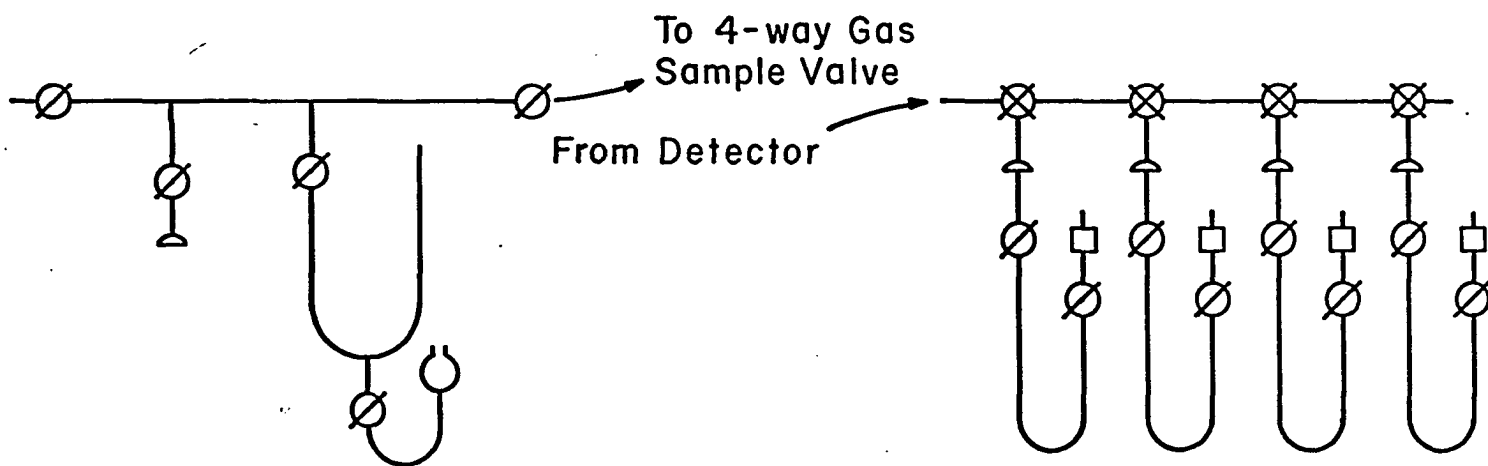


Figure II-B - Low-Pressure Fractionating Column



- ⊗ Three-way Stopcock
- ⊘ Two-way Stopcock
- One-way Check Valve

Figure II-C - Inlet and Collection Systems for the Gas Chromatograph

connections to the Swagelock fittings of the instrument were made using Teflon ferrules. A sample loop of Pyrex glass (volume ~8 cc.) was constructed for the 4-way valve and was attached in the same way as the manifold.

In actual operation, a sample was transferred from the vacuum line to the inlet system by means of a glass tube fitted with a stopcock and ground glass joint. Once the volume between the stopcocks on the tube and manifold had been evacuated, the sample was allowed to expand into the sample loop and injected into the column by operating the gas sampling valve. The collection traps (Figure II-D) were kept at -196° and the path of the effluent gases was controlled by means of the 3-way stopcocks on the collection manifold. On completion of the separation, the collection traps maintained at -196° were transferred to the vacuum line. After evacuation of noncondensable materials, the samples were pumped into the line through two traps immersed in liquid nitrogen.

The columns used in the various separations are listed in Table II-1. Each column was heated overnight at its maximum allowable temperature prior to use.

Helium flow was adjusted to approximately 100 cc./sec., with an inlet pressure of 50 lb./sq.in., while the detector at 7.5 volts was fixed at 50° greater than the column temperature. The injector was not heated. A Sargent 1 m.v. recorder, Model SR, was used to monitor the detector.

5. Pressure Measurements

All pressure measurements were made with a two-column open-end mercury manometer which could be read accurately to within 0.01 mm. with the aid of a cathetometer.

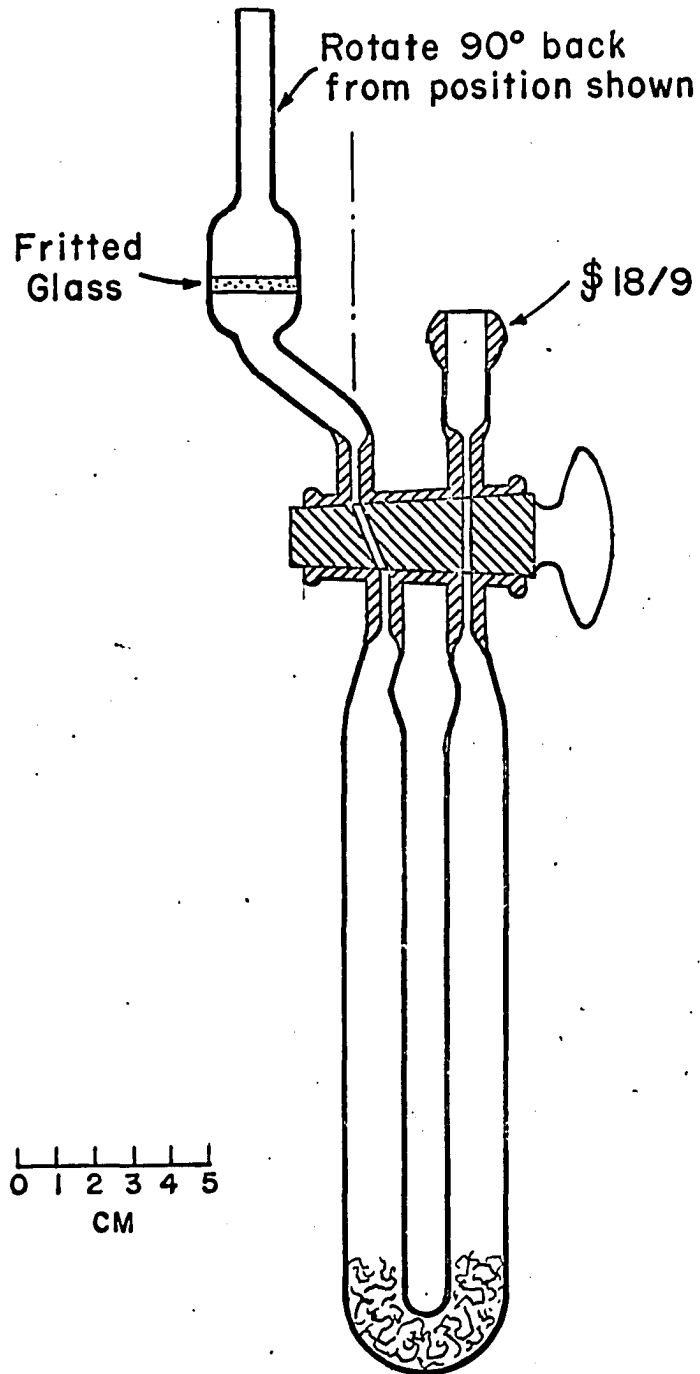


Figure II-D - Collection Trap for the Gas Chromatograph

Table II-1
Gas Chromatography Columns

Code	Column Material	Length	Liquid Phase ^a	Support ^b	Tmax, °C
A	3/8" Al	18'	Silicone 710	Chromasorb W	225
B	3/8" Al	20'	Silicone 710	Firebrick	225
C	3/8" Al	20'	Carbowax 400	Chromasorb W	100
D	1/4" Cu	15'	Squalane	Chromasorb W	30
G	1/4" Cu	15'	Benzyl Ether	Chromasorb W	80
H	1/4" Glass	5'	Benzyl Ether	Chromasorb W	80

^a All columns were loaded with 20 w/w% liquid phase.

^b 60-80 mesh support used for all columns.

6. Temperature Measurements

Accurate temperatures were measured using an iron-constantan or copper-constantan thermocouple in conjunction with a potentiometer (Gray Instrument Company, Model E-3067), with ice-water (0.0°) as a reference junction. Accurate temperature measurement was required for vapor pressure and molecular weight determinations. All other temperature measurements were made using standard mercury or pentane thermometers. Temperatures will be reported here in degrees Centigrade (°C).

7. Production of Low Temperatures

Low temperatures in this research were obtained primarily by the utilization of liquid nitrogen both directly, to provide a temperature of -196°, and indirectly, to cool various organic liquids to their characteristic slush point temperatures. The liquids used, along with their melting points, boiling points and flammabilities, are listed in Table II-2. In addition, a dry ice-isopropanol slurry provided a temperature of -78°.

8. Molecular Weight Determinations

Two methods were used in determining molecular weights of pure compounds. The first was the standard Dumas method for samples in the gas phase using the ideal gas law $pV = nRT$.

The second and more accurate method was the precise mass measurement of the parent ion peak, if present, using an Associated Electrical Industries MS9 Double Focusing High Resolution Mass Spectrometer. The "peak matching" method measures mass usually to within 0.001 atomic mass unit.

Table II-2
Low Temperature Baths

Bath Temperature (°C)	Bath Material	Boiling Point (°C)	Flammability
5.5	Benzene	80	+
0.0	Water-ice	100	-
- 6	Cyclohexane	83	+
- 23	Carbon Tetrachloride	76	-
- 31	Bromobenzene	155	+
- 36	Ethylene Dichloride	84	+
- 45	Chlorobenzene	132	+
- 50	Diethyl Malonate	199	-
- 64	Chloroform	61	-
- 84	Ethyl Acetate	77	+
- 96	Toluene	112	+
-111	Freon 11	23	-
-116	Ethyl Ether	35	+
-120	Ethyl Bromide	38	-
-126	Methylcyclohexane	100	+
-134	n-Pentane	36	+
-145	iso-Butane	- 10	+
-160	iso-Pentane	28	+

9. Melting Point Determination

Whenever possible, melting points were determined by means of a Stock magnetic plunger device.¹⁸¹

10. Infrared Spectra

All infrared spectra were recorded on a Perkin-Elmer model 457 Grating Infrared Spectrometer. The instrument is self-calibrating and a periodic calibration using the 1601 cm^{-1} band of the polystyrene spectrum revealed a variance of less than 1%.

Gas phase samples were contained in a cell with a length of 10 cm. fitted with 6 mm. thick KBr windows. The windows were attached to the cell with glyptal resin.

11. Nuclear Magnetic Resonance Spectra

Nuclear magnetic resonance spectra were recorded on either a Hitachi Perkin-Elmer model R-20 High Resolution NMR Spectrometer (60 MHz.), a Varian Associates model HA-100 Proton Stabilized NMR Spectrometer (100 MHz.) or a 250 MHz. PMR spectrometer. The last two spectrometers were located at the NIH Facility for Biomedical Research at Mellon Institute (Grant No. RR 00292). The R-20 spectra were calibrated by the side-band method and graphical interpolation. The side-bands were produced by a Hewlett-Packard 3300A Function Generator monitored by a Takeda Riken TR3824X Frequency Counter. The HA-100 spectra were calibrated by using the monitor control switch in the DIFF 1 position. In this position, the difference between the manual oscillator frequency (determined by the position of the lock) and the swept oscillator frequency (determined by the position of the pen) is displayed on the instrument's frequency counter. Any mark of the pen could therefore be read directly as Hz. from the lock signal. The HA-100 was also operated

in connection with a Varian model V-4311 Variable Temperature accessory.

12. Mass Spectra

Mass spectra were obtained using an Associated Electrical Industries MS9 Double Focusing High Resolution Mass Spectrometer. Two different ionizing beam voltages were generally used: 70 electron volts and approximately 12 electron volts. At the lower voltage, fragmentation is decreased and the parent peak enhanced. The instrument was also used for precise mass measurement (section 8).

13. Vapor Pressure Curves

A vapor pressure curve (vapor pressure versus temperature) was plotted for new compounds whenever possible. The data were substituted into the equation

$$\log P = -\frac{A}{T} + B$$

where P is the pressure at temperature T ($^{\circ}$ K), A represents the slope of the line and B is a constant. The data were analyzed by means of a computer program for least squares analysis. The computer program provides a plot of the experimental points and the best straight line through them. The computer also derives the heat of vaporization, the extrapolated boiling point, Trouton's constant and the calculated vapor pressure of the compound at the temperatures of commonly used cold baths.

14. Criteria of Purity

The purity of the materials prepared in the course of this research was confirmed by at least one of the following criteria. The purity of new compounds was substantiated by as many as possible.

- a. Gas phase molecular weight, to within 1% of the calculated value.

- b. Mass measurement, to within 0.001 mass units of the calculated mass.
- c. Infrared spectrum, compared with a published spectrum or with a spectrum of a sample of known purity.
- d. Fragmentation pattern of low voltage mass spectrum, useful in determining if any impurity or mixture is present.
- e. Vapor pressure, to within 1% for compounds found in the literature.
- f. Gas chromatography, a single peak generally indicative of a pure sample.

B. Reagents and Starting Materials

1. Commercially Available Reagents

Acetic Acid - (Baker) used as received.

Acetone - (Baker) distilled prior to use, boiling point 57°.

Stored over type 4A molecular sieves.

Allyl Bromide - (Fisher) used as received.

Allyltrichlorosilane - (Peninsular Chemresearch) used as received.

Ammonia - (Air Products) distilled from sodium.

Ammonium Thiocyanate - (Baker) used as received.

Chloroacetonitrile - (Eastman) distilled prior to use, boiling point 123°. Dried and stored over type 4A molecular sieves.

Chloromethyl Methyl Sulfide - (Columbia Organic Chemicals)

Purified by vacuum line distillation: R.T. → -78° →
-96° → -196°.

Di-n-Butyl Ether - (Matheson) distilled from sodium prior to use, boiling point 141°.

1,1-Dichloroethane - (Eastman) distilled from calcium hydroxide prior to use, boiling point ~57°. Stored over type 4A molecular sieves.

1,2-Dichloroethane - (Baker) distilled from calcium hydroxide prior to use, boiling point 83°-84°. Stored over type 4A molecular sieves.

Dimethylchlorosilane - (Peninsular Chemresearch) used as received.

Dimethylformamide - (Eastman) distilled prior to use, boiling point $\sim 152^\circ$. Dried and stored over type 4A molecular sieves.

Dimethylsulfoxide - (Baker) distilled from calcium hydride prior to use, boiling point 189° .

Germanium Dioxide - supplied by Germanium Research Institute. Used as received.

Hexamethylphosphortriamide - (Fisher) distilled from calcium hydride at reduced pressure, boiling point $\sim 110^\circ$ at 5 torr. Stored over type 4A molecular sieves.

Lithium Aluminum Hydride - (Metal Hydrides) used as received.

Phosphorus Pentafluoride - (Air Products) purified by vacuum line distillation: R.T. $\longrightarrow -134^\circ \longrightarrow -196^\circ$; mol. wt. found 126.6, calc. 126.0; infrared spectrum was identical to published spectrum.¹⁴⁷

Potassium Thiocyanate - (Baker) used as received.

Silver Cyanide - (Fisher) used as received.

Silver Thiocyanate - (Eastman) used as received.

Sodium Borohydride - (Fisher) used as received.

Sodium Cyanide - (Baker) used as received.

Trifluoroethyl Chloride - (K & K) used as received.

Vinyl Bromide - (Peninsular Chemresearch) used as received.

2. Synthesized Reagents

Allylsilane

Allylsilane was prepared by the reduction of commercially available

allyltrichlorosilane with lithium aluminum hydride in di-n-butyl ether.¹¹² The crude product was distilled in the vacuum line: R.T. \longrightarrow -84° \longrightarrow -120° \longrightarrow -196° . Identity and purity of the product was confirmed by mass spectrometry.

Chloromethylsilane

This compound was prepared by the reduction of commercially available chloromethyltrichlorosilane with lithium aluminum hydride in di-n-butyl ether.¹¹² The crude product was distilled: R.T. \longrightarrow -23° \longrightarrow -116° \longrightarrow -196° . Identity of the product was confirmed by its infrared spectrum.¹⁶

Germane

Germane was prepared by the reduction of germanium dioxide by sodium borohydride.¹⁰⁹ Potassium hydroxide (8 g.), germanium dioxide (4 g.) and sodium borohydride (4.2 g.) were added successively to 100 ml. of water, stirring for a few hours to attain maximum dissolution. The solution was added dropwise to approximately 400 ml. glacial acetic acid in a 1-liter 3-neck flask, which had been flushed with nitrogen, allowing 10-15 minutes for the addition. The pressure in the flask was maintained between 10-20 torr by evacuating through traps at -78° and -196° . The resulting gas in the -196° trap was distilled: R.T. \longrightarrow -134° \longrightarrow -196° to remove digermane, trigermane and some carbon dioxide. The remaining carbon dioxide was removed by repeated passage of the impure germane through an ascarite column. The infrared spectrum of the resulting product was identical to the published spectrum.¹⁸¹ The purity was checked by molecular weight measurement (found 76.6, calc. 76.64).

Iodomethylsilane

Iodomethylsilane was prepared by condensing chloromethylsilane and acetone into a flask containing excess sodium iodide and refluxing gently (35°-40°) for 1.5-2 hours.¹⁶ The crude product was distilled: R.T. → -64° → -196°. The infrared spectrum of the product was identical to the published spectrum.¹⁶

Silyl Bromide

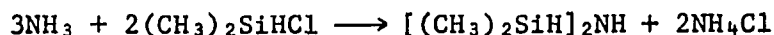
Silyl bromide was kindly donated by Dr. G. A. Gibbon.

1,1,1',1'-Tetramethyldisiloxane

This compound was prepared by reacting $(\text{CH}_3)_2\text{SiHCl}$ with excess degassed water at room temperature.^{70,204} The crude product was purified by vacuum distillation: R.T. → -64° → -196°.

1,1,1',1'-Tetramethyldisilylamine

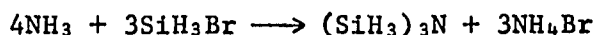
The preparation of this compound was achieved by the reaction



Ammonia (3.5 millimoles) and excess dimethylchlorosilane (3.5 millimoles) were placed in a 0.2 liter and 3-liter flask respectively. The flasks were connected to each other and to the vacuum line by means of a T-tube. After evacuation of the T-tube, the stopcocks on the flasks were opened, resulting in quick and complete mixing of the gases. (If excess NH_3 is permitted, the formation of $(\text{CH}_3)_2\text{SiHNH}_2$ is facilitated.)¹⁸² After five minutes at room temperature, the volatile products were vacuum distilled: R.T. → -45° → -196°. The purity was checked by molecular weight determination (found 132.2, calc. 133.31).

Trisilylamine

Trisilylamine was prepared by the reaction:¹⁸²



The procedure was similar to that described for tetramethyldisilylamine. The $(\text{SiH}_3)_3\text{N}$ formed in the reaction was purified by vacuum line distillation: R.T. \longrightarrow -78° \longrightarrow -96° \longrightarrow -196° . The infrared spectrum of the product was identical with the published spectrum.^{61,155} The identity and purity were further confirmed by mass spectrometry.

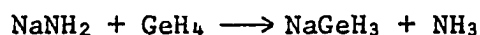
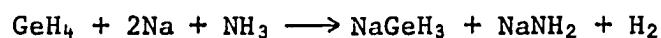
C. The Preparation and Characterization of Some New Organogermanes

1. Preparation and Properties of 1,2-Digermylethane

a. Procedure

(1) Preparation of Sodium Germyl

A known amount of sodium (151 mg., 6.6 millimoles) was introduced into a reaction vessel (Figure II-A). The flask was evacuated and immersed in a -78° temperature bath. Approximately 30 ml. of freshly dried and distilled ammonia was condensed into the flask, commencing dissolution of the sodium. A slight excess of germane (6.9 millimoles) was condensed into the flask by maintaining a liquid nitrogen-saturated cotton swab against the flask's outer wall. The characteristic deep blue color of the Na-NH_3 solution began to appear lighter and after approximately one hour the solution had changed to a pale yellow color, indicating that the sodium had completely reacted with the germane. It has been shown that the reaction takes place in two steps:¹⁶¹



An excess of germane is used in order to ensure the complete conversion of NaNH_2 . Reactions were facilitated by cooling the reaction vessel to -196° after an initial reaction period of up to an hour, removing the hydrogen and rewarming to -78° . Removal of ammonia after completion of

the reaction was accomplished by evacuating overnight while maintaining the flask at -78° . The next day, evacuation was continued for an hour with the flask at -23° .^a The resulting NaGeH_3 was a dry, white powder.

(2) Reaction of Sodium Germyl and 1,2-Dichloroethane

Into the reaction vessel containing the freshly prepared sodium germyl was condensed 1,2-dichloroethane (289 mg., 2.9 millimoles). The flask was allowed to warm to room temperature for ~20 hours. At the end of the reaction period, a small amount of noncondensable gases, presumably hydrogen, was removed. The volatile products were distilled: R.T. \longrightarrow -45° \longrightarrow -96° \longrightarrow -196° . Infrared data of the -96° fraction indicated that it was composed of a mixture of digermane,⁴⁹ ethylgermane,¹³¹ and 1,2-digermylethane. Final purification of the latter compound was accomplished by gas chromatography (see below). The total weight of pure 1,2-digermylethane collected was 135.5 mg. (45% yield).

b. Gas Chromatography

The mixture of compounds composing the -96° fraction mentioned above was separated on the gas chromatograph. Conditions used were: column A, column temperature = 106° , detector temperature = 149° , flow rate = 105 ml./min. The resulting peaks and their retention times, t_r , are listed in Table II-3.

^a Evacuation must be continued for an extended period, for the NaGeH_3 originally crystallizes as $\text{NaGeH}_3 \cdot 6\text{NH}_3$. The ammonia of crystallization is then removed in stages: $\text{NaGeH}_3 \cdot 6\text{NH}_3$, $\text{NaGeH}_3 \cdot 4.5\text{NH}_3$, $\text{NaGeH}_3 \cdot 2\text{NH}_3$, and NaGeH_3 .¹¹⁹

Table II-3
Retention Times for the G. C. Separation of $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$
from Impurities

t_r (minutes)	Assignment
<6.5	$\text{GeH}_3\text{CH}_2\text{CH}_3$
7.35	Ge_2H_6
15.0	$\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$
23.1	$\text{ClCH}_2\text{CH}_2\text{Cl}$

c. Gas Phase Molecular Weight

The molecular weight was determined by the standard Dumas method and found to be 178.4 (calc. 179.28).

d. Precise Mass Measurement

A precise mass measurement was conducted on two peaks in the parent ion region. The results are summarized in Table II-4.

Table II-4
Precise Mass Measurement Data for $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$

Ion (empirical formula)	Measured Mass	Calculated Mass
$^{72}\text{Ge}^{70}\text{GeC}_2\text{H}_6$	171.8918	171.8933
$^{72}\text{Ge}_2\text{C}_2\text{H}_6$	173.8915	173.8911
$^{74}\text{Ge}^{70}\text{GeC}_2\text{H}_6$	173.8915	173.8924

e. Melting Point

The melting point of 1,2-digermylethane, determined by the Stock method,¹⁸¹ was -60.4° .

f. Vapor Pressure

The vapor pressure of $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ was determined at various temperatures in the range -25° to $+5^\circ$. The glass manometer system had been pretreated with an impure sample of 1,2-digermylethane for a period of about 16 hours. A least squares computer analysis of the observed temperature and pressure values provided the data contained in Tables II-5 and II-6 and Figure II-E. At the conclusion of the vapor pressure determination the infrared spectrum was identical with that of the pure material.

g. Thermal Stability

A sample of $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ was sealed in a breakseal tube and allowed to remain at room temperature for several days. Solid material did not form on the breakseal walls and the infrared spectrum was unchanged at the conclusion of the experiment.

Table II-5
Vapor Pressure of 1,2-Digermylethane

Exptl. Press.	Temp. (°C)	Calc. Press.	Calc.Press.-Exptl.Press.
<u>Increasing Temperature</u>			
7.25	-23.8	6.85	-.40
7.40	-22.6	7.41	.01
8.00	-21.6	7.90	-.10
8.21	-20.8	8.34	.13
9.01	-19.0	9.29	.28
10.13	-17.3	10.35	.22
10.71	-17.0	10.54	-.17
11.39	-15.5	11.56	.17
12.52	-13.8	12.81	.29
19.02	- 7.0	19.09	.07
20.79	- 5.4	20.87	.08
25.29	- 2.0	25.27	-.02
28.30	- 0.2	27.88	-.42
34.27	+ 3.4	33.82	-.45
<u>Decreasing Temperature</u>			
20.00	- 6.8	19.36	-.64
18.55	- 8.2	17.85	-.70
14.52	-12.7	13.72	-.80
10.67	-16.2	11.09	.42
^a All pressures given in millimeters of mercury.			

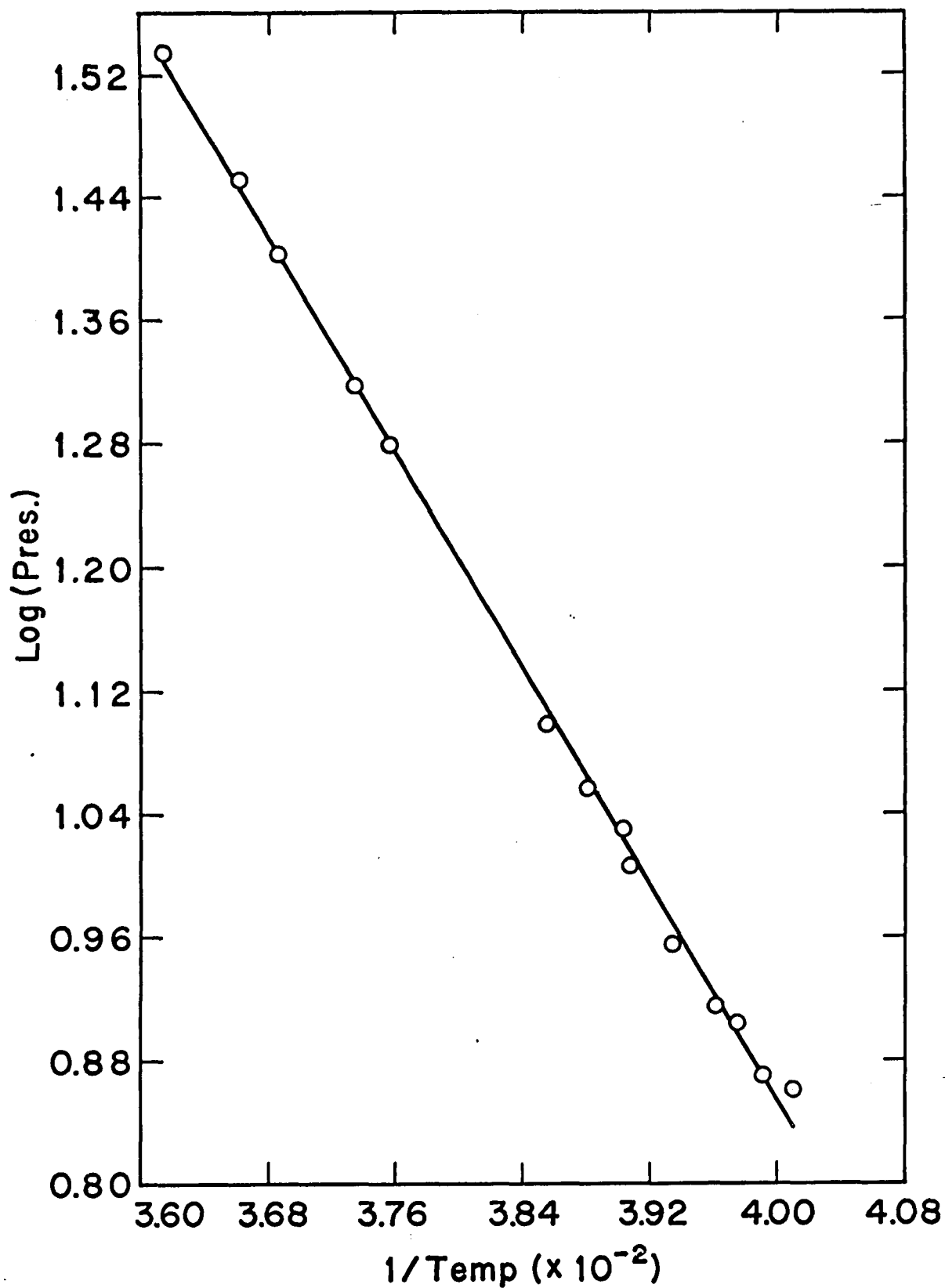


Figure II-E - Vapor Pressure of $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$

Table II-6

Data for $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ Derived from Vapor Pressure Plot

Slope = -1757.92	Heat of Vaporization = 8044.12 cal. mole ⁻¹
Intercept = 7.88554	Trouton's Constant = 22.90 cal. mole ⁻¹ deg. ⁻¹
Boiling Point = 78.09°C	Sum Square = .0602

h. Infrared Spectrum

The infrared spectrum of $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ was recorded in the gas phase at pressures of 5 torr and 15 torr and is shown in Figure II-F. It has been shown by infrared and Raman spectroscopy that the starting material, 1,2-dichloroethane, exists in the trans (C_{2h}) and gauche (C_2) forms in the gaseous state.¹³⁹ The infrared spectrum in Figure II-F indicates that the same is probably true for this compound. The band assignments for $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ are listed in Table II-7 as well as the possible rotamer from which each band is generated.

Table II-7

Infrared Absorption Frequencies of $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$

Absorption (cm^{-1})	Intensity ^a	Assignment ^a	Probable Conformer ^b	Reference
2935	m	$\nu_a(\text{CH})$	g,t	190
2912	m	$\nu_s(\text{CH})$	g,t	190
2835	w	unassigned	--	
2074	s	$\nu_s, \nu_s(\text{GeH}_3)$	g,t	34,50,91,131
1425	w	$\delta_a, \delta_s(\text{CH}_2)$	g,t	50,131,139,158
1297				
1290	w	w(CH_2)	g	139
1283				

Table II-7 (Continued)

Absorption (cm^{-1})	Intensity ^a	Assignment ^a	Probable Conformer ^b	Reference
1237 1228	mw	w(CH ₂)	t	131,139
1145	w	t(CH ₂)	g,t	139
1073	mw	ν (C-C)	g,t	131,139
890 883	sh m	δ_a, δ_s (GeH ₃)	g,t	91,131
853	m	ρ (CH ₂)	g	139
830	s	δ_s (GeH ₃)	g,t	91,131
788 782	mw	ρ (CH ₂)	t	139,190
732 723	m	ρ (CH ₂)	g	131,190
700	mw	ρ (CH ₂)	t	190
626 618	mw	ν (Ge-C)	t	131,190
608 603	m	ν (Ge-C)	g	91,190
558	m	unassigned	--	
507	w	ρ (GeH ₃)	?	91,131
489	w	ρ (GeH ₃)	?	131

^a For explanation of symbols, see Appendix.

^b g = gauche, t = trans

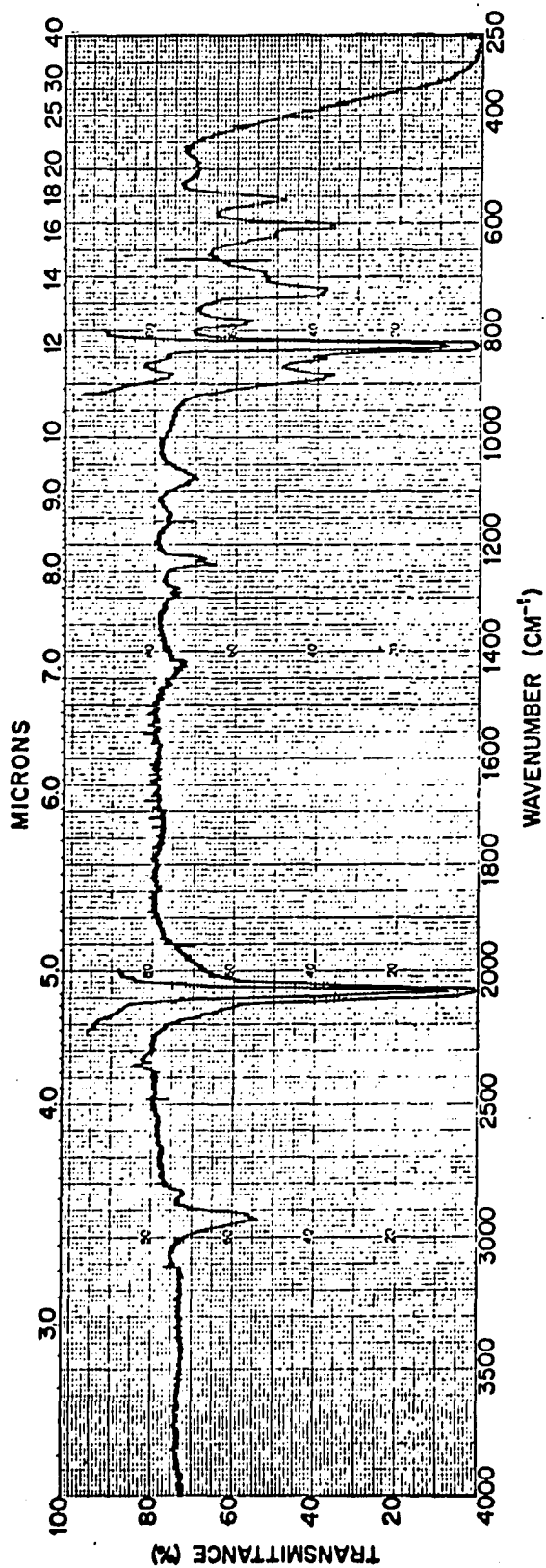


Figure II-F - Infrared Spectrum of $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$

1. Proton Magnetic Resonance Spectrum

The proton magnetic spectrum of $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ was measured on the 100 MHz. spectrometer at a concentration of 10% by volume in deuteriochloroform using 2% tetramethylsilane as an internal standard. The spectrum consisted of two sets of peaks, which are shown in Figures II-G and II-H. The spectrum appears to be simple, consisting of a septet centered at 8.84 τ , assigned to the CH protons, and a quintet at 6.43 τ , assigned to the GeH protons. However, the situation is most likely complicated by the strong coupling which occurs between the four methylene protons, usually termed "virtual coupling".¹⁵ The result is that the germyl protons do not produce a simple quartet, as might be expected from a first order analysis, but a multiplet of at least seven lines. The methylene proton pattern is also probably more complex than the simple quintet. However, the distance between the peaks in each of the patterns was exactly 1.8 Hz., and this value was taken as reflective of the CH-GeH coupling constants. The data are summarized in Table II-8.

Table II-8

Proton Magnetic Resonance Data for $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$

Proton Environment	Chemical Shift ^a	Relative Intensity ^b	$J_{\text{CH-GeH}}$ ^c
CH ₂	8.84	2	1.8
GeH ₃	6.43	3	1.8

^a Values reported according to the τ scale.

^b Determined by planimeter.

^c Values reported in Hz.

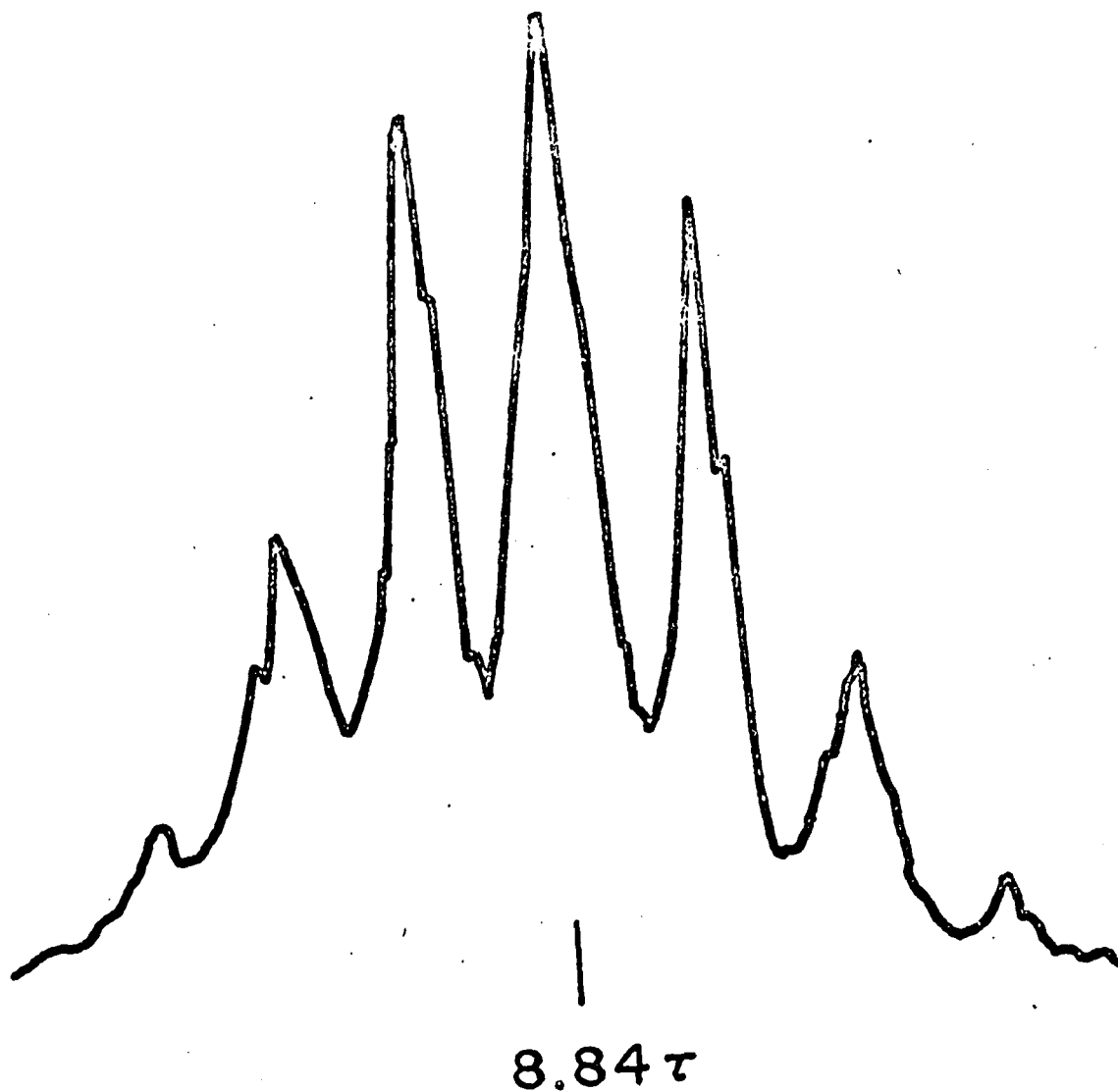


Figure II-G - CH_2 Proton Resonance at 50 Hz. Sweep Width
(for $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$)

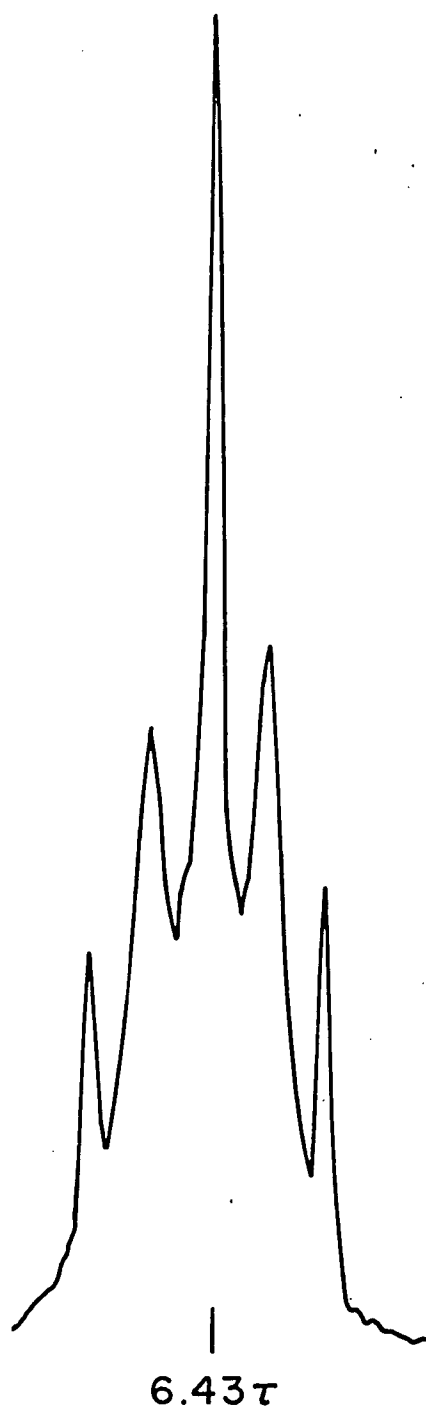


Figure II-H - GeH_3 Proton Resonance at 50 Hz. Sweep Width
(for $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$)

j. Mass Spectrum

The mass spectrum of $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ is very complex. This is true for all germyl compounds, owing to the existence of five germanium isotopes in significant natural abundance. These are: isotope (percent); ^{70}Ge (20.5); ^{72}Ge (27.4); ^{73}Ge (7.8); ^{74}Ge (36.5); ^{76}Ge (7.8). In addition, there is the possibility of rupturing a variable number of the hydrogen-germanium bonds that are present in the compound, leading to formation of ions containing from zero to the maximum number of hydrogen atoms. These complications prevent the assignment of each peak to a specific ion. The data are therefore presented in two tables: Table II-9 contains a list of the m/e values for all major peaks and their relative intensities; Table II-10 follows the method suggested by Ebsworth and co-workers, which considers groups of peaks due to ions with a common heavy-atom skeleton.⁴⁵ Thus the group Ge_2C_2^+ refers to all ions between 164 ($^{70}\text{Ge}_2^{12}\text{C}_2^+$) and 188 ($^{76}\text{Ge}_2^{12}\text{C}_2^1\text{H}_{10}^+$). Relative intensities are obtained by normalizing the total intensities of each group, imparting to the most abundant fragment an assigned intensity of 100.

An interesting observation is the presence of the group Ge_2^+ with fairly large intensities. The obvious explanation of digermene present as an impurity can be discarded. The product collected from the gas chromatograph was detected as a single peak and neither infrared nor magnetic resonance detected any trace of digermene. It has been suggested instead that the ion is formed as part of the fragmentation processes, implying that the bonding electrons are redistributed quite readily.⁴⁵

Table II-9

Observed Fragmentation Pattern for $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$

m/e	Relative Intensity (%) ^a	m/e	Relative Intensity (%) ^a	m/e	Relative Intensity (%) ^a
184	1.1	155	5.9	104	41.5
183	2.1	154	15.0	103	90.7
182	4.5	153	18.2	102	26.7
181	7.3	152	27.0	101	74.3
180	7.0	151	35.8	100	17.4
179	10.5	150	41.2	99	14.1
178	11.7	149	38.7	98	10.2
177	13.4	148	45.4	97	17.2
176	11.6	147	33.8	96	7.0
175	13.1	146	32.4	95	10.5
174	9.5	145	20.0	77	57.2
173	6.9	144	18.6	76	24.1
172	6.1	143	8.2	75	60.6
171	3.1	142	6.2	74	36.4
170	2.1	141	4.4	73	48.6
169	2.2	140	2.4	72	22.7
167	1.0	107	19.6	71	21.4
157	1.1	106	6.9	70	14.0
156	3.5	105	100.0		

^a Only those peaks greater than 1% relative intensity are presented.

Table II-10

Group Mass Peak Assignments for $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$

Heavy Atom Skeleton	Relative Intensity (%)
C_2Ge_2^+	25.9
Ge_2^+	82.1
C_2Ge^+	100.0
Ge^+	65.3

2. Preparation and Properties of 1,1-Digermylethanea. Preparation

Sodium germyl was prepared as described previously (page 41). Germane (15.2 millimoles) reacted with a solution of sodium (283 mg., 12.30 millimoles) in liquid ammonia until the blue Na-NH_3 solution changed to a pale yellow. The ammonia was removed by evacuating for 16 hours at -78° , then 2 hours at -23° . 1,1-dichloroethane (604.0 mg., 6.10 millimoles) was condensed into the reaction flask and warmed to 0° for 24 hours, after which hydrogen was removed and the volatile products were distilled: $\text{R.T.} \rightarrow -84^\circ \rightarrow -111^\circ \rightarrow -134^\circ \rightarrow -196^\circ$. The lowest temperature fraction contained mainly GeH_4 , as identified by its infrared spectrum.¹⁸⁰ Infrared evidence was also used to determine that the -134° fraction consisted of $\text{CH}_3\text{CH}_2\text{GeH}_3$ ¹³¹ and the -111° fraction of Cl_2CHCH_3 . The fraction collected in the highest temperature trap contained Cl_2CHCH_3 plus a compound with a strong Ge-H stretching frequency, presumably the desired 1,1-digermylethane, and was further purified by gas chromatography (see below).

A second sample was prepared as described above using 9.8 millimoles

of germane, 213 mg. (9.26 millimoles) of sodium and 433.6 mg. (4.38 millimoles) of 1,1-dichloroethane. The reaction proceeded for 48 hours at 0°. The total weight of gas chromatograph-purified product from the second reaction was 2.7 mg. (0.5% yield).

b. Gas Chromatography

The -84° fraction of each sample was purified on the gas chromatograph. Conditions used were: column A, column temperature = 90°, detector temperature = 150°, flow rate = 100 ml./min. The resulting peaks and their retention times, t_r , are listed in Table II-11.

Table II-11

Retention Times for the G. C. Separation of $(\text{GeH}_3)_2\text{CHCH}_3$
from Impurities

t_r (minutes)	Assignment
14.30	$\text{GeH}_3\text{CH}_2\text{CH}_3$
16.40	Cl_2CHCH_3
20.42	$(\text{GeH}_3)_2\text{CHCH}_3$

d. Precise Mass Measurement

A precise mass measurement was performed on three peaks in the parent ion region of a mass spectrum obtained of the initial sample. The results are tabulated in Table II-12.

Table II-12
Precise Mass Measurement Data for $(\text{GeH}_3)_2\text{CHCH}_3$

Ion (empirical formula)	Measured Mass	Calculated Mass
${}^{74}\text{Ge}_2\text{C}_2\text{H}_6$	177.8895	177.8893
${}^{72}\text{Ge}{}^{74}\text{GeC}_2\text{H}_8$	177.9050	177.9059
${}^{72}\text{Ge}_2\text{C}_2\text{H}_{10}$	177.9224	177.9216

e. Melting Point

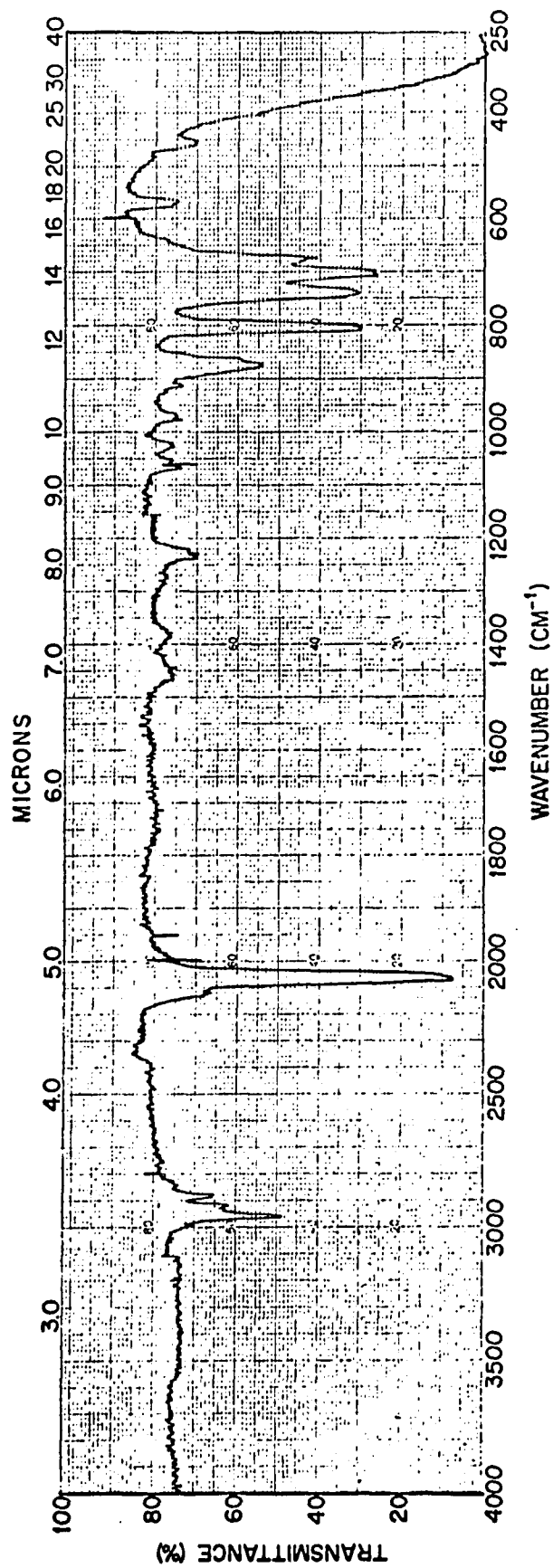
A melting point determination using the Stock method¹⁸¹ was conducted on the 20.42 minute fraction obtained from the gas chromatographic purification of the second sample. The measured value of -4.8° was considerably higher than expected from the initial vacuum line behavior of the compound and lends support to the instability of the compound.

f. Infrared Spectrum

An infrared spectrum of the 20.42 minute fraction of the second sample was recorded in the gas phase at a pressure of 15 torr and is given in Figure II-I. No attempt was made to assign all the absorption frequencies. It can be stated with reasonable certainty, however, that the bands at 2960, 2920, 2886 and 2878 are due to C-H stretching frequencies^{91,131} and the bands at 2074 and 2064 arise from Ge-H stretching frequencies.^{91,93,131}

g. Proton Magnetic Resonance Spectrum

The proton magnetic resonance spectrum was obtained on the two samples after purification by gas chromatography. Each sample was

Figure II-I - Infrared Spectrum of $(\text{GeH}_3)_2\text{CHCH}_3$

run in deuteriochloroform with 5% tetramethylsilane added as an internal standard.

Both samples were run on the 250 MHz. spectrometer at very low concentrations. In the first sample, a doublet ($J_1 = 3.3$ Hz.) of quartets ($J_3 = 0.5$ Hz.) centered at 6.29τ was assigned to the GeH_3 protons. A doublet ($J_2 = 8.0$ Hz.) of septets ($J_3 = 0.5$ Hz.) centered at 8.62τ was assigned to the CH_3 protons. The CH proton was unobserved, most likely due to its low intensity. In addition, J_1 , J_2 and J_3 were assumed to be the coupling constants of the $\text{GeH}_3\text{-CH}$, $\text{CH}_3\text{-CH}$ and $\overline{\text{GeH}_3\text{-CH-CH}_3}$ protons respectively.

Unfortunately, the second sample produced equivocal results. Two separate doublets were observed at 2.71 and 7.96τ with coupling constants of 25.5 and 6.0 Hz. respectively. A triplet at 6.90τ with a coupling constant of 4.0 Hz. was also present. In addition, a group of six lines of variable intensity was observed in the vicinity of 8.85τ .

The signals observed in the first case concur with the expected spectrum and probably reflect the true values of the $(\text{GeH}_3)_2\text{CHCH}_3$ spectrum. In the second case, thermal decomposition must have occurred,^a producing the observed spectrum.

^a It should be noted that the nuclear magnetic resonance spectrum for the second sample was recorded after various manipulations in the vacuum line. Hopefully, no decomposition occurred prior to the infrared and melting point measurements. However, there is the possibility that decomposition did occur and that the infrared and melting point measurements may not have been determined on extremely pure samples.

h. Mass Spectrum

A mass spectrum was obtained on the initially prepared sample at an ionizing voltage of 70 electron volts. The fragmentation data are listed in Table II-13. The complications which arise due to the presence of five appreciable germanium isotopes and the several germanium hydrogen bonds in the molecule have been discussed previously (page 53). Table II-14 contains data derived using the heavy atom skeleton method.⁴⁵

Note should be taken of the intensity of the Ge_2^+ ion. The occurrence of this ion in 1,2-digermylethane was explained as facility in redistributing the bonding electrons. In that case, however, the compound was shown to be thermally stable with a very small probability for the presence of Ge_2H_6 . In the present case, the evidence indicates a thermally unstable compound and the presence of digermene is a very distinct possibility. The amplitude of the peaks in this portion of the mass spectrum may very likely be due to Ge_2H_6 arising from the instability of the desired compound.

Table II-13

Observed Fragmentation Pattern for $(\text{GeH}_3)_2\text{CHCH}_3$

m/e	Relative Intensity ^a (%)	m/e	Relative Intensity ^a (%)	m/e	Relative Intensity ^a (%)
184	5.2	158	2.4	106	16.6
183	5.6	157	4.1	105	45.5
182	13.4	156	4.0	104	74.3
181	13.5	155	5.8	103	66.2
180	27.7	154	14.6	102	69.2
179	22.3	153	19.0	101	19.9
178	35.3	152	44.4	100	79.6
177	25.5	151	48.7	99	21.2
176	29.8	150	83.6	98	59.4
175	15.9	149	72.8	97	8.6
174	22.5	148	100.0	79	5.7
173	10.7	147	79.7	78	4.0
172	9.3	146	84.2	77	70.4
171	4.4	145	55.8	76	23.2
170	3.8	144	54.8	75	38.6
169	3.0	143	24.1	74	71.0
167	2.0	142	18.3	73	28.4
163	2.6	141	8.4	72	53.3
161	3.8	140	5.7	71	14.7
160	2.4	107	10.6	70	37.5
159	3.7				

^a Only those peaks greater than 1% relative intensity are presented.

Table II-14

Group Mass Peak Assignments for $(\text{GeH}_3)_2\text{CHCH}_3$

Heavy Atom Skeleton	Relative Intensity (%)
Ge_2C_2^+	34.3
Ge_2C^+	2.1
Ge_2^+	100.0
GeC_2^+	68.0
Ge^+	47.8

3. Preparation and Properties of 3-Germylpropene

3-Germylpropene is a previously known compound, having been prepared by the reduction of $\text{CH}_2=\text{CHCH}_2\text{GeCl}_3$ with lithium hydride.¹⁴⁵ However, the compound was only partially characterized. An alternate method of preparation is described here and certain properties of the compound have been determined.

a. Preparation

Sodium germyl was prepared, as described previously, by reacting GeH_4 (5.7 millimoles) with a solution of Na (113 mg., 4.9 millimoles) in liquid ammonia at -78° until the blue Na-NH_3 solution changed to clear. The ammonia was removed by evacuating for ~ 16 hours at -78° , then 2 hours at -23° . Allyl bromide (10 millimoles) was introduced by maintaining a liquid nitrogen saturated cotton swab on the outer wall of the reaction vessel. After 6 hours at 0° , the white NaGeH_3 had changed to an orange-yellow color. Hydrogen was removed and the volatile products were distilled: $\text{R.T.} \longrightarrow -96^\circ \longrightarrow \underline{-134^\circ} \longrightarrow -196^\circ$. The -196° fraction consisted of germane, identified by its infrared

spectrum.¹⁸⁰ The -134° fraction consisted of 3-germylpropene, while the -96° fraction was mainly unreacted allyl bromide. Final purification was accomplished by gas chromatography (see below). The total weight of pure product collected was approximately 75 mg. (15% yield).

b. Gas Chromatography

The -134° fraction was purified using the gas chromatograph. Conditions used were: column A, column temperature = 100° , detector temperature = 150° , flow rate = 101 ml./min. The peaks collected and their retention times, t_r , are listed in Table II-15.

Table II-15

Retention Times for the G. C. Separation of $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$
from Impurities

t_r (minutes)	Assignment
9.18	$\text{CH}_2=\text{CHCH}_2\text{GeH}_3$
19.48	$\text{CH}_2=\text{CHCH}_2\text{Br}$

c. Gas Phase Molecular Weight

The gas phase molecular weight was determined by the standard Dumas method and found to be 118.0 (calc. 116.64).

d. Precise Mass Measurement

A precise mass measurement was performed on one of the peaks in the parent ion region. The measured mass (115.9689) corresponded to an empirical formula of $\text{C}_3\text{H}_6^{74}\text{Ge}$ (calc. 115.9681).

Table II-16
 Vapor Pressure of 3-Germylpropene^a

Exptl. Press.	Temp. (°C)	Calc. Press.	Calc.Press.-Exptl.Press.
<u>Increasing Temperature</u>			
6.17	-58.0	5.89	- .28
11.34	-48.5	11.49	.15
14.02	-45.5	14.04	.02
17.38	-41.6	18.06	.68
24.22	-36.4	24.95	.73
25.01	-36.0	25.56	.55
28.54	-34.2	28.48	- .06
31.31	-32.6	31.31	.00
31.90	-32.3	31.87	- .03
35.02	-31.0	34.38	- .64
39.68	-28.8	39.02	- .66
41.06	-27.7	41.54	.48
48.42	-24.8	48.84	.42
55.53	-22.6	55.09	- .44
78.58	-16.2	77.29	-1.29
86.01	-14.4	84.76	-1.25
<u>Decreasing Temperature</u>			
21.10	-39.4	20.74	- .36
15.43	-43.4	16.09	.66

^a All pressures given in millimeters of mercury.

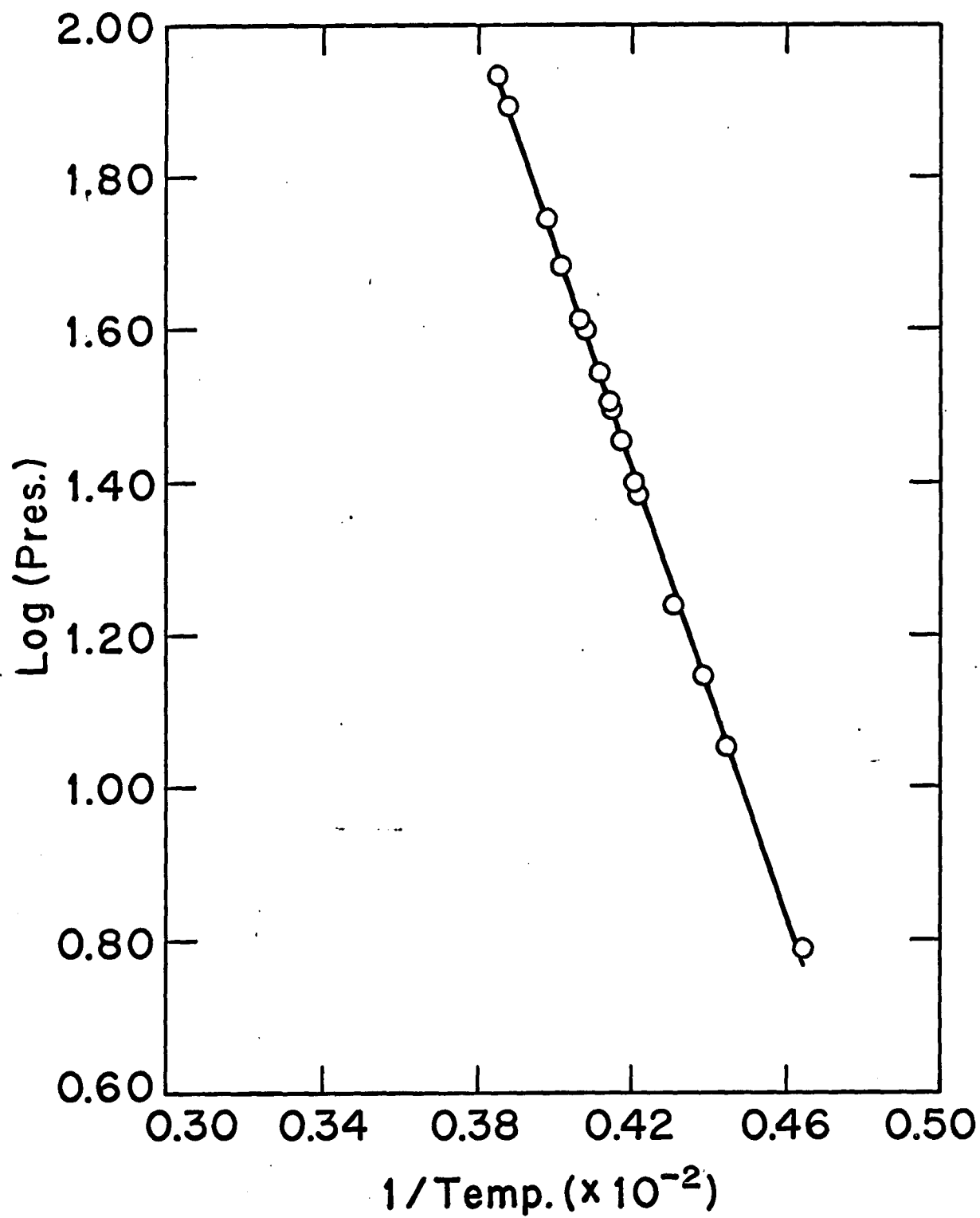


Figure II-J - Vapor Pressure of $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$

Table II-17

Data for $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$ Derived from Vapor Pressure Plot

Slope = -1479.19	Heat of Vaporization = 6768.67 cal. mole ⁻¹
Intercept = 7.64462	Trouton's Constant = 21.80 cal. mole ⁻¹ deg. ⁻¹
Boiling Point = 37.35°C	Sum Square = .3791

e. Vapor Pressure

The vapor pressure of $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$ was determined at several temperatures in the range -60° to -10° . The glass manometer system had been pretreated with an impure sample of the substance for a period of about 16 hours. A least squares computer analysis of the observed temperatures and pressures provided the data in Tables II-16 and II-17 and Figure II-J.

f. Infrared Spectrum

The infrared spectrum of $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$ in the gas phase was recorded at pressures of 7 torr and 53 torr. The spectrum is shown in Figure II-K and the band assignments are listed in Table II-18.

g. Proton Magnetic Resonance

The proton magnetic resonance was obtained from a sample of $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$ which was 20 v/v% in deuteriochloroform. Approximately 2% of tetramethylsilane was added as an internal reference. Figure II-L is a spectrum obtained on the 60 MHz. spectrometer at a sweep width of 600 Hz. An expanded spectrum is given in II.G.(page 115) and is further discussed in III.C.(page 153).

h. Mass Spectrum

A mass spectrum was obtained at an ionizing voltage of

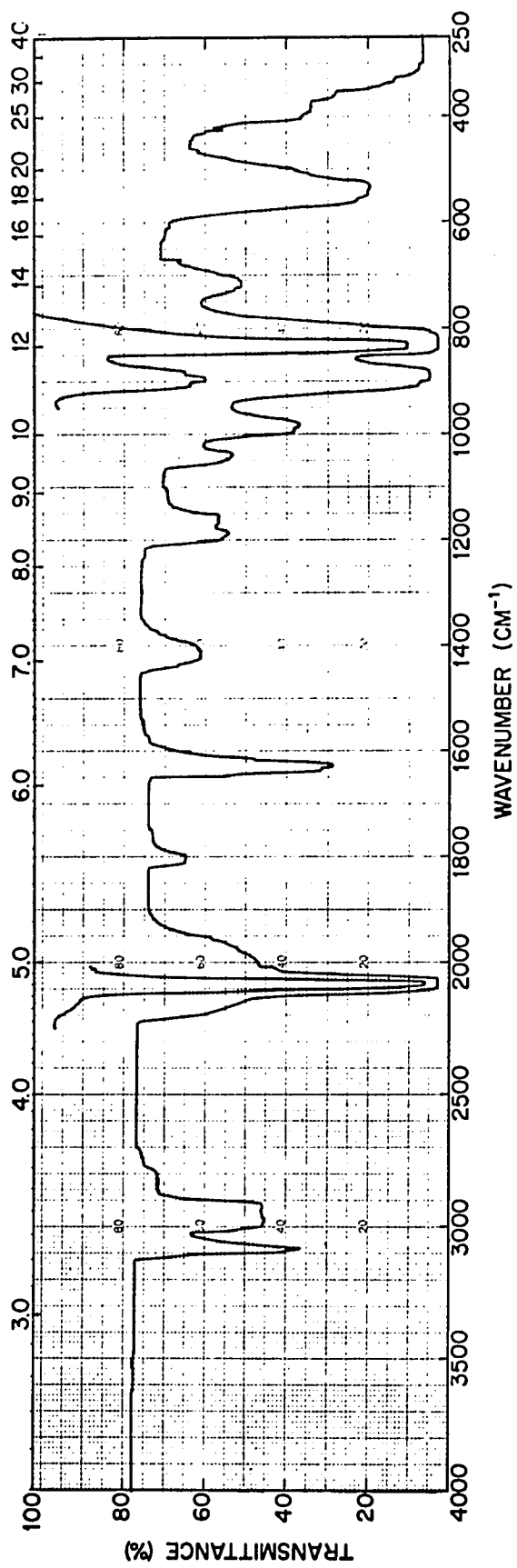


Figure II-K - Infrared Spectrum of $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$

Table II-18
Infrared Absorption Frequencies of $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$

Absorption (cm^{-1})	Intensity ^a	Assignment ^a	Reference
3092	m	$\nu_a(\text{CH}_2=)$	11,74,94
2978	m	$\nu_s(\text{CH}_2=)$	94
2912	m	$\nu_s(\text{CH}_2)$	74,94
2080	vs	$\nu_a, \nu_s(\text{GeH}_3)$	91,131
1806	w	897 + 910 = 1807	
1628	m	$\nu(\text{C}=\text{C})$	11,73,94
1415	w	$\delta(\text{CH}_2), \delta(\text{CH})$	94
1188	mw	w(CH_2)	94
1166 1155	mw	t(CH_2)	94
1040	mw	$\nu(\text{C}-\text{C})$	74,131,158
995 983	m	$\delta(\text{CH}_2)$	74
910 897 883	vs	$\delta_a(\text{GeH}_3)$	91,131
833	vs	$\delta_s(\text{GeH}_3)$	91,131
718	mw	$\rho(\text{CH}_2)$	131
540	ms	$\nu(\text{Ge}-\text{C})$	73
390 380	m	$\delta(\text{C}=\text{C}-\text{C})$	94

^a For explanation of symbols, see Appendix.

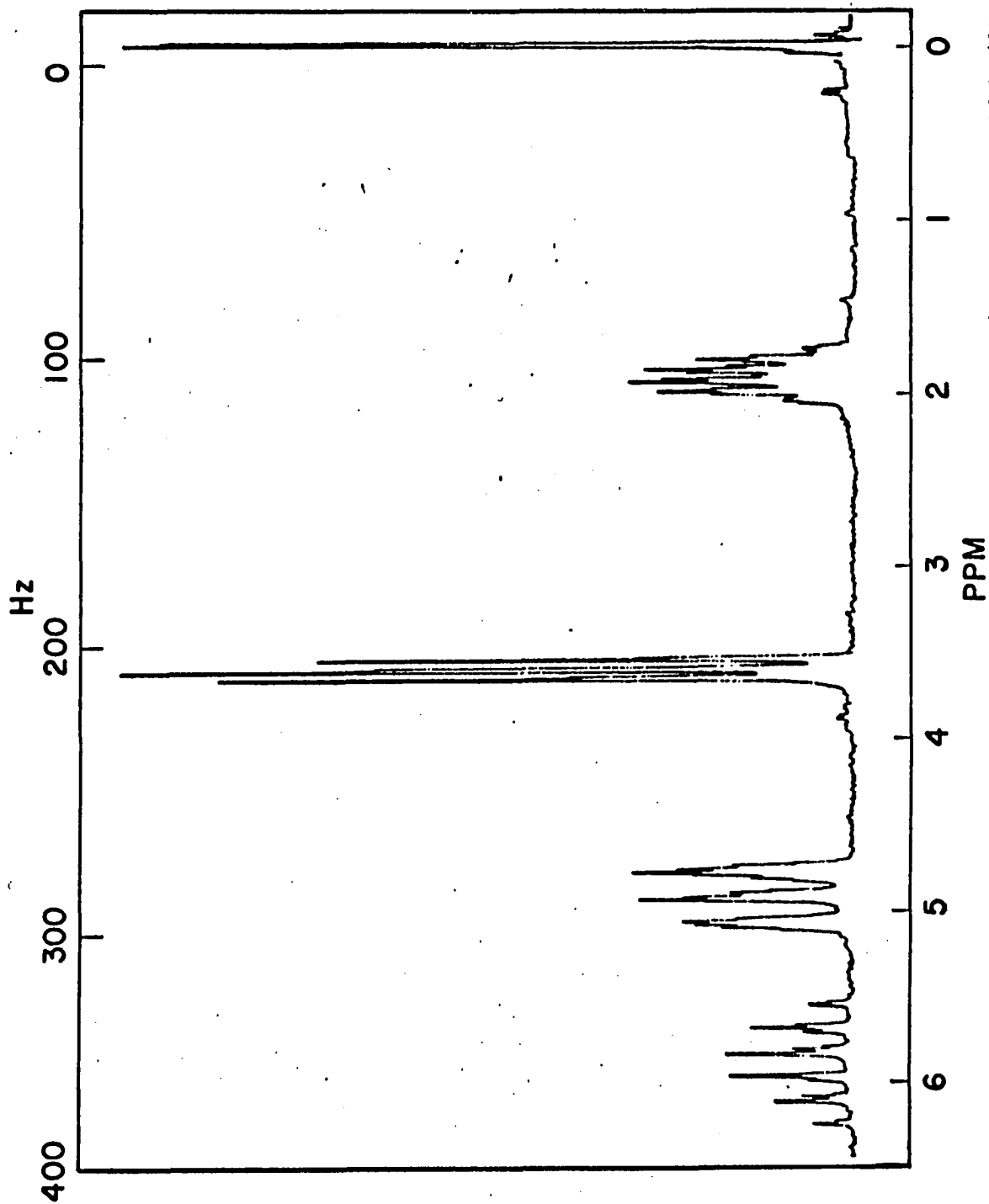


Table II-19

Observed Fragmentation Pattern for $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$

m/e	Relative Intensity ^a (%)	m/e	Relative Intensity ^a (%)	m/e	Relative Intensity ^a (%)
119	6.2	102	4.2	84	12.6
118	12.9	101	16.2	77	25.8
117	6.7	100	4.2	76	32.8
116	24.8	99	16.0	75	48.5
115	9.1	98	7.2	74	100.0
114	22.1	97	14.5	73	51.0
113	18.1	96	7.2	72	76.5
112	18.8	95	6.7	71	23.6
111	20.0	91	14.2	70	56.5
110	9.7	90	11.8	41	62.7
109	8.3	89	72.3	40	10.8
108	6.6	88	40.6	39	82.3
105	4.1	87	55.8	38	11.0
104	4.2	86	18.0	27	15.1
103	8.8	85	37.8	26	6.6

^a Only those peaks greater than 1% relative intensity are presented.

70 electron volts. The resulting fragmentation is listed in Table II-19. Complications arising from the presence of five appreciable germanium isotopes and the several germanium-hydrogen bonds in the molecule have been discussed earlier (page 53). Table II-20 contains data derived using the heavy atom skeleton method.⁴⁵

Table II-20

Group Mass Peak Assignments for $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$

Heavy Atom Skeleton	Relative Intensity (%)
C_3Ge^+	39.4
C_2Ge^+	22.5
CGe^+	63.5
Ge^+	100.0
C_3^+	40.2
C_2^+	5.2

4. Preparation and Properties of Germylmethyl Methyl Sulfide

a. Procedure

(1) Preparation of Potassium Germyl

Approximately 30 ml. of hexamethylphosphortriamide (HMPT) was placed in a reaction vessel (Figure II-A) and degassed by evacuating the flask at $\sim 60^\circ$. The flask was cooled below 10° , opened, and freshly cut potassium (44.5 mg., 11.4 millimoles) added. Dissolution began immediately, exhibiting the characteristic dark blue color. The flask was quickly returned to the vacuum line and evacuated. Germane (12.4 millimoles) was allowed to expand into the flask, which was maintained below 10° . After being permitted to proceed for several minutes, the reaction was facilitated by opening the flask to the pump through a -196° trap, removing any hydrogen formed and recondensing the germane into the reaction vessel. The solution soon turned a pale yellow, indicating that the potassium had completely reacted with the

germane to form KGeH_3 . Excess germane was removed by evacuating once more through a -196° trap.

(2) Reaction of Potassium Germyl and Chloromethyl Methyl Sulfide

Chloromethyl methyl sulfide (1.23 g., 11.9 millimoles) was condensed into the reaction vessel containing the freshly prepared solution of KGeH_3 in HMPT. The reaction mixture was maintained between 0° and 10° for 1 hour. Hydrogen was removed and the volatile products were distilled: R.T. \rightarrow -96° \rightarrow -196° . Infrared data of the -96° fraction indicated a compound containing a Ge-H bond, presumably the desired germylmethyl methyl sulfide. Final purification of the mixture was accomplished by gas chromatography (see below).

b. Gas Chromatography

The -96° fraction was purified using the gas chromatograph. Conditions used were: column H, column temperature = 32° , detector temperature = 92° , flow rate = 100 ml./min. The peaks collected and their retention times, t_r , are listed in Table II-21.

Table II-21
Retention Times for the G. C. Separation of $\text{GeH}_3\text{CH}_2\text{SCH}_3$
from Impurities

t_r (minutes)	Assignment
16.50	$\text{GeH}_3\text{CH}_2\text{SCH}_3$
22.48	$\text{ClCH}_2\text{SCH}_3$

c. Precise Mass Measurement

A precise mass measurement was performed on one of the peaks

in the parent ion region. The measured mass (133.9599) corresponded to an empirical formula $C_2H_8^{70}GeS$ (calc. 133.9589).

d. Vapor Pressure, Melting Point and Thermal Stability

A vapor pressure determination was initiated but discontinued when it was observed that the vapor pressure continually decreased at constant temperature.

A melting point determination, using the Stock method,¹⁸¹ yielded a temperature of -8.5° , which seemed high considering the behavior of the compound during routine vacuum line manipulations. The melting point apparatus was immersed in a -23° temperature bath and was opened to a -196° trap. The material condensing in the trap had a spectrum identical to that of the material identified as $GeH_3CH_2SCH_3$. The material remaining in the melting point apparatus had an extremely low vapor pressure, insufficient to generate enough material for an infrared spectrum, and a high viscosity at room temperature.

It was concluded that the thermal stability of $GeH_3CH_2SCH_3$ is quite low and that the compound forms a relatively high melting polymer of low vapor pressure.

e. Infrared Spectrum

In the gas phase, $GeH_3CH_2SCH_3$ seemed to be more stable than in the liquid phase. Furthermore, the product remaining after decomposition, as noted above, lacked sufficient vapor pressure to produce an infrared spectrum. It was therefore possible to obtain a satisfactory gas phase infrared spectrum at pressures of 5 torr and 25 torr. The spectrum is shown in Figure II-M and the band assignments are listed in Table II-22.

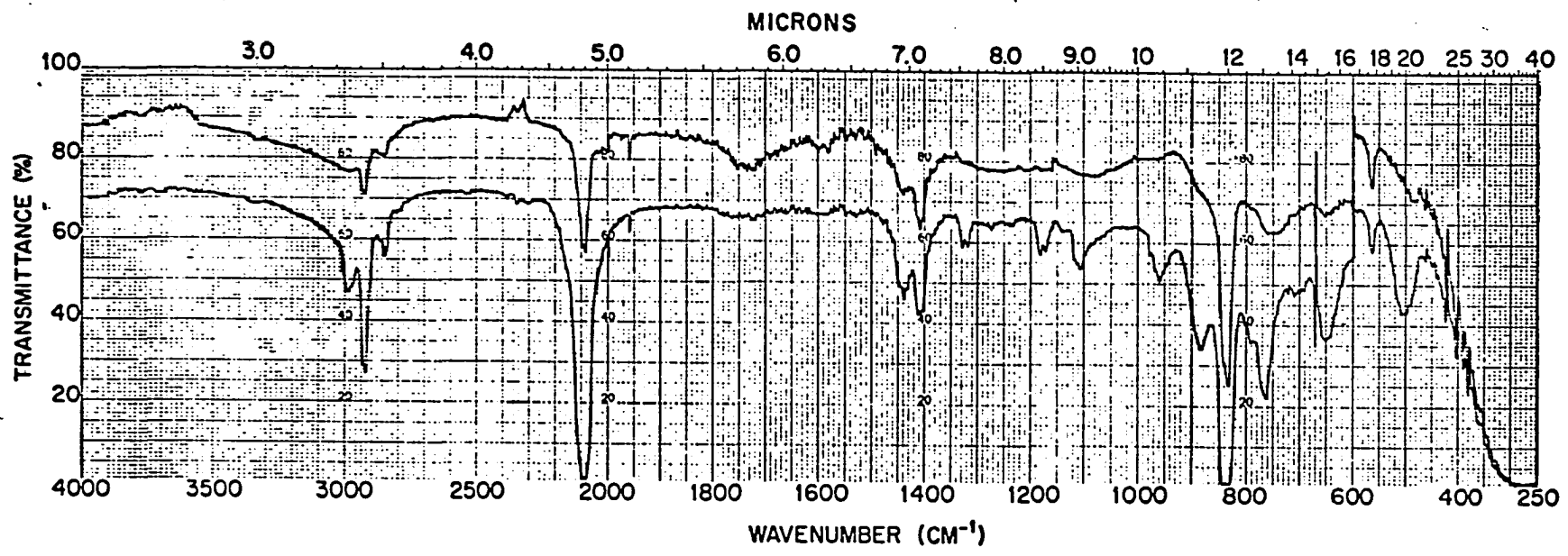


Figure II-M - Infrared Spectrum of $\text{GeH}_3\text{CH}_2\text{SCH}_3$

Table II-22
Infrared Absorption Frequencies of $\text{GeH}_3\text{CH}_2\text{SCH}_3$

Absorption (cm^{-1})	Intensity ^a	Assignment ^a	Reference
2990	mw	$\nu_a(\text{CH}_3)$	91
2932 2924	m	$\nu_s(\text{CH}_2)$	87,131
2852	w	$\nu_s(\text{CH}_3)$	87
2094 2083	vs	$\nu_a, \nu_s(\text{GeH}_3)$	91,131
1439	m	$\delta_a(\text{CH}_2), \delta_a(\text{CH}_3)$	91,87,96,131,190
1409	m	$\delta_s(\text{CH}_2)$	190
1329 1318	w	$\delta_s(\text{CH}_3)$	87,96,171
1182 1172	w	$\tau(\text{CH}_2)$	139
960	mw	$\rho(\text{CH}_3)$	96,171
883	m	$\delta_a, \delta_s(\text{GeH}_3)$	131
840 834	s	$\delta_s(\text{GeH}_3)$	91,131
793	msh	$\rho(\text{CH}_2)$	96
762	m	$\rho(\text{CH}_2)$	96,131,171
650	m	$\nu(\text{Ge-C})$ $\nu(\text{C-S})$	17,87,96,115,171, 190
502	m	$\rho(\text{GeH})$	91,131

^a For explanation of symbols, see Appendix.

f. Proton Magnetic Resonance Spectrum

The reaction products obtained from a 1:1 reaction between $\text{CH}_3\text{SCH}_2\text{Cl}$ and KGeH_3 were purified by means of the low-pressure fractionating column (Figure II-B). The fraction presumed to contain $\text{GeH}_3\text{CH}_2\text{SCH}_3$ was sealed in a standard 5 mm. nmr tube and the proton magnetic spectrum was measured on the 250 MHz. spectrometer at a concentration of 6 v/v% in deuteriochloroform using ~3% tetramethylsilane as an internal standard. The spectrum consisted of five sets of peaks, which are shown in Figure II-N. Two of the five, however, (at 5.29 τ and 7.71 τ) are derived from $\text{ClCH}_2\text{SCH}_3$, as the proton magnetic spectrum of a pure sample of this latter compound revealed. The remaining three groups of lines may be assigned to $\text{GeH}_3\text{CH}_2\text{SCH}_3$. The singlet at 7.82 τ arises from the CH_3 protons. The GeH_3 protons split by methylene protons are the source of the triplet at 6.26 τ , while the quartet at 7.87 τ originates from the CH_2 protons split by the three germyl protons. The data are summarized in Table II-23.

Table II-23

Proton Magnetic Resonance Data for $\text{GeH}_3\text{CH}_2\text{SCH}_3$

Proton Environment	Chemical Shift ^a	Relative Intensity ^b	$J_{\text{CH}_2-\text{GeH}_3}$ ^c
CH_3	7.82	3	--
CH_2	7.87	2	3.37
GeH_3	6.26	3	3.37

^a Values reported according to the τ scale.

^b Measured by planimeter.

^c Values reported in Hz.

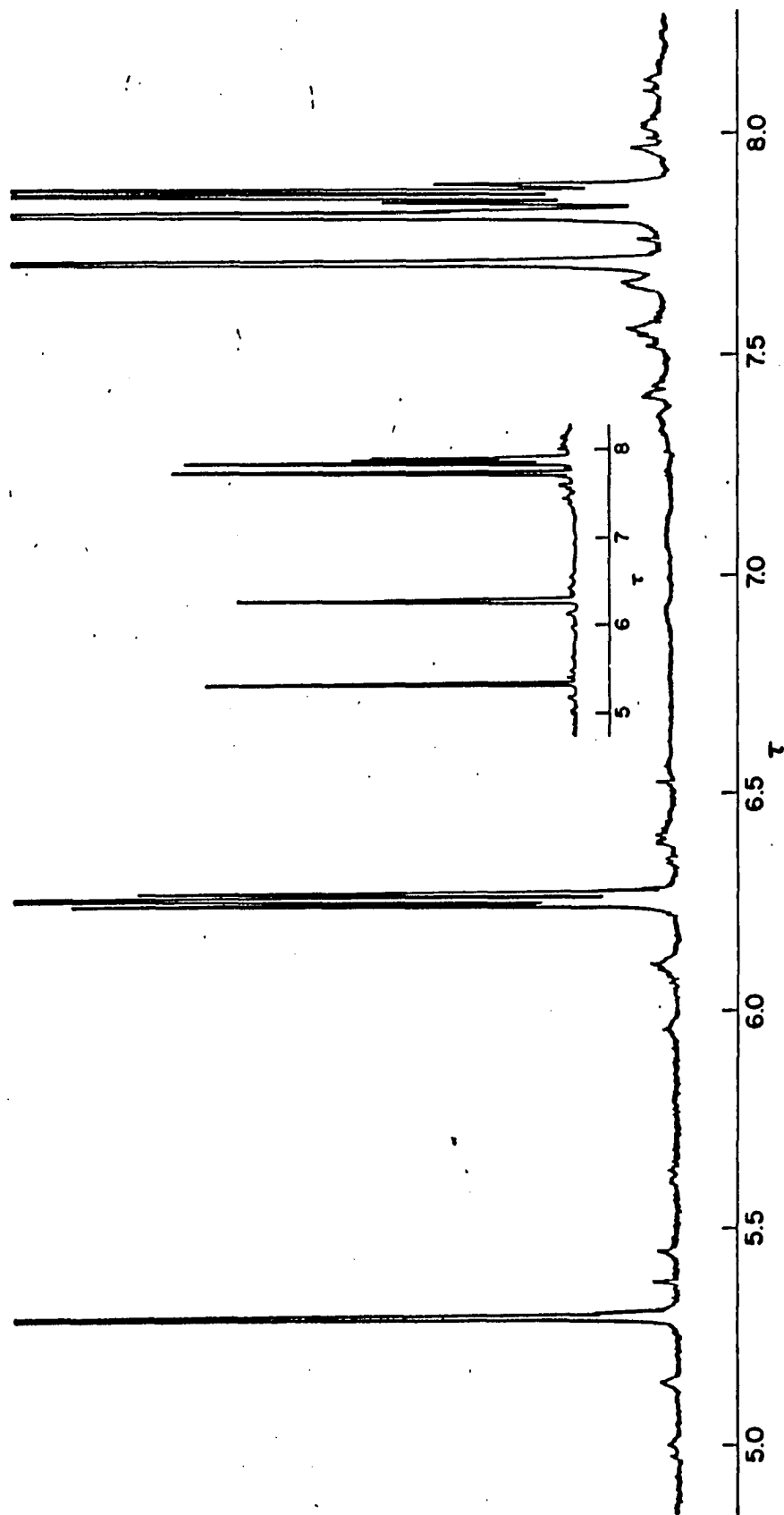


Figure II-N - Proton Magnetic Resonance Spectrum of $\text{GeH}_3\text{CH}_2\text{SCH}_3$ Plus $\text{ClCH}_2\text{SCH}_3$ Impurity (250 MHz.)

Table II-24

Observed Fragmentation Pattern for $\text{GeH}_3\text{CH}_2\text{SCH}_3$

m/e	Relative Intensity ^a (%)	m/e	Relative Intensity ^a (%)	m/e	Relative Intensity ^a (%)
140	8.7	119	26.2	76	3.8
139	2.5	118	4.3	75	10.0
138	32.2	117	34.4	74	9.2
137	13.4	116	2.1	73	9.2
136	27.3	115	3.3	72	6.7
135	13.4	91	1.9	71	4.3
134	20.7	90	3.8	70	4.6
133	9.6	89	14.1	63	15.1
132	1.1	88	8.5	62	9.0
131	5.6	87	11.2	61	100.0
125	2.9	86	5.6	47	40.5
123	24.6	85	7.0	46	2.4
122	4.6	84	2.6	45	15.6
121	30.6	77	3.8	44	5.7
120	9.0				

^a Only those peaks greater than 1% relative intensity are presented.

g. Mass Spectrum

A mass spectrum was obtained at an ionizing voltage of 70 electron volts. The resulting fragmentation is listed in Table II-24. Complications arising from the presence of 5 appreciable germanium isotopes

Table II-25

Group Mass Peak Assignments for $\text{GeH}_3\text{CH}_2\text{SCH}_3$

Heavy Atom Skeleton	Relative Intensity (%)
C_2GeS^+	94.1
CGeS^+	100.0
CGe	38.2
Ge^+	36.0
C_2S^+	86.9
CS^+	45.0

and the several germanium-hydrogen bonds in the molecule are dealt with as described earlier (page 53). Table II-25 contains data derived from the heavy atom skeleton method.⁴⁵

D. The Reaction of Alkali Metal Derivatives of Germane with Vinyl Bromide, 1,2-Dichloroethene, 1,1,1-Trifluoro-2-chloroethane, and Chloroacetonitrile

1. Reaction of Sodium Germyl with Vinyl Bromide

Summary: An excess of vinyl bromide was found to react with solid sodium germyl at 0° to produce a small quantity of vinyl germane. The yield was too small to consider the reaction a convenient method for preparing this compound.

Experiment A: Approximately 25 ml. of dry liquid ammonia was distilled into the reaction vessel (Figure II-A) containing freshly cut sodium (193 mg., 8.4 millimoles). Germane (8.8 millimoles) was introduced until the blue Na-NH_3 solution maintained at -78° changed to a

clear, pale yellow and evolution of hydrogen ceased. The ammonia was removed by evacuating the flask overnight at -78° , then for 2 hours at -23° . Vinyl bromide (13.1 millimoles) was condensed into the flask and allowed to react with the solid sodium germyl for ~ 16 hours at 0° . After a small amount of hydrogen was removed, the volatile products were distilled: R.T. $\longrightarrow -120^{\circ} \longrightarrow -134^{\circ} \longrightarrow -196^{\circ}$. The -196° fraction was identified by its infrared spectrum as GeH_4 .¹⁸⁰ The -134° fraction was injected into the gas chromatograph using column A at a temperature of 50° and a flow rate of 109 ml./sec. Materials collected at retention times of 8.66 min. and 16.22 min. were identifiable from their infrared and mass spectra as vinyl germane²⁸ and vinyl bromide respectively. The yield ($\sim 0.05\%$) is small enough to discourage consideration of this reaction as a convenient preparation of vinyl germane, although suitable conditions may be discovered which would lead to an increased yield.

2. The Reaction of Sodium Germyl with 1,1,1-Trifluoro-2-chloroethane

Summary: Equimolar quantities of solid NaGeH_3 and $\text{CF}_3\text{CH}_2\text{Cl}$ were found to interact at 0° and -23° to form CF_3CH_3 , GeH_4 and Ge_2H_6 . A flask containing the same starting materials and allowed to warm from -196° while opened to a trap immersed in liquid nitrogen formed only a small amount of GeH_4 .

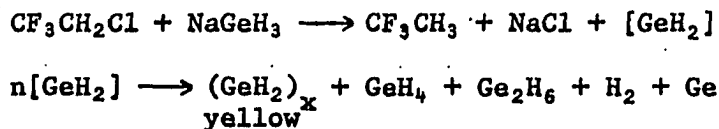
Experiment A: Approximately 20 ml. of dried liquid ammonia was condensed into a reaction vessel (Figure II-A) containing freshly cut sodium (82.4 mg., 3.6 millimoles). Germane (5.0 millimoles) was introduced into the flask maintained at -78° until the blue color of the Na-NH_3 solution changed to a clear, pale yellow and evolution of hydrogen had ceased. The ammonia was removed by evacuating the flask overnight at -78° , then for 2 hours at -23° . $\text{CF}_3\text{CH}_2\text{Cl}$ (3.7 millimoles) was

condensed into the flask by applying a liquid nitrogen-saturated cotton swab to the outside of the flask. The chloride was allowed to interact with the solid NaGeH_3 for 4 hours at room temperature. During the course of the reaction, the white NaGeH_3 changed to yellow-orange. An appreciable amount of hydrogen was removed after which the volatile products were distilled: R.T. \longrightarrow -111° \longrightarrow -134° \longrightarrow -196° . The -196° fraction was identified as GeH_4 ,¹⁸⁰ the -134° fraction as Ge_2H_6 ,⁴⁹ and the -111° fraction as a mixture of CF_3CH_3 and unreacted $\text{CF}_3\text{CH}_2\text{Cl}$ on the basis of infrared and mass spectra.

Experiment B: 9.55 millimoles of solid sodium germyl was prepared as above. $\text{CF}_3\text{CH}_2\text{Cl}$ (8.0 millimoles) was condensed into the reaction vessel and allowed to warm to -23° for 5 hours. Separations and identification were essentially the same as previously described. The reaction yielded CF_3CH_3 , GeH_4 , and Ge_2H_6 with unreacted $\text{CF}_3\text{CH}_2\text{Cl}$ also present.

Experiment C: $\text{CF}_3\text{CH}_2\text{Cl}$ (4.3 millimoles) was condensed into the reaction vessel containing solid NaGeH_3 (4.3 millimoles) and allowed to warm from -196° to room temperature while open to a trap maintained at -196° . Any $\text{CF}_3\text{CH}_2\text{GeH}_3$ formed would immediately condense into the trap, allowing minimum time for decomposition to occur. The procedure was repeated 5 times; each time material from the trap was recondensed into the reaction vessel. During the course of the reaction, the white NaGeH_3 changed to orange-brown. A trace of volatile products was collected and identified as GeH_4 .¹⁸⁰

In general, the reaction appears to proceed as follows:



If the compound $\text{CF}_3\text{CH}_2\text{GeH}_3$ is formed, it appears to decompose very readily under the conditions employed.

3. Reaction of Sodium Germyl with cis-1,2-Dichloroethene

Summary: $\text{ClCH}=\text{CHCl}$ was reacted with a large excess of solid NaGeH_3 at 0° for 6.5 hours. Other reactions at room temperature for longer times were initiated. The starting dichloride was recovered unchanged in each case.

Experiment A: Dried liquid ammonia (25 ml.) was condensed into a reaction vessel (Figure II-A) containing freshly cut sodium (206 mg., 8.86 millimoles). Germane (10.03 millimoles) was introduced until the blue Na-NH_3 solution maintained at -78° changed to a clear, pale yellow and evolution of hydrogen had ceased. The ammonia was removed by evacuating the flask overnight at -78° , then for 1.5 hours at -23° . Degassed 1,2-dichloroethene (2.49 millimoles) was condensed into the flask and allowed to react with the solid NaGeH_3 at 0° for 6.5 hours. The volatile products were distilled from the flask: $0^\circ \rightarrow -78^\circ \rightarrow -134^\circ \rightarrow -196^\circ$ and no hydrogen was detected. The -196° fraction contained GeH_4 (0.4 millimoles) identified by its infrared spectrum. A trace of $\text{GeH}_3\text{CH}_2\text{CH}_3$ appeared in the -134° fraction but the majority of both the -78° and -134° fractions was unreacted $\text{ClCH}=\text{CHCl}$. Experiments were performed using similar reactant ratios for up to three days at room temperature. Distillations similar to those described yielded similar results.

4. Reaction of Sodium Germyl with Chloroacetonitrile

Summary: Chloroacetonitrile and solid sodium germyl in a 1:1 molar ratio were allowed to react at 0° . The resulting volatile products

consisted of germane and digermane. No evidence was provided for any compound containing both Ge-H and C-N bonds.

Experiment A: Dried liquid ammonia (~25 ml.) was condensed into a reaction flask (Figure II-A) containing freshly cut sodium (106 mg., 4.6 millimoles). Germane (4.2 millimoles) was introduced into the flask until the blue Na-NH₃ solution maintained at -78° had changed to a clear, pale yellow. The ammonia was removed by evacuating the flask at -78° overnight, then at -23° for 2 hours. Degassed ClCH₂CN (345 mg., 4.6 millimoles) was condensed into the flask and allowed to react with the solid NaGeH₃ at 0° for one hour. Hydrogen gas was detected and removed, after which the volatile products were distilled: 0° → -64° → -134° → -196°. The -196° fraction consisted of GeH₄ as determined by its infrared spectra.²⁰⁶ The -134° fraction contained a small amount of Ge₂H₆, as shown by mass spectral identification. The -64° fraction was entirely unreacted ClCH₂CN.⁴⁹

E. The Fluorination of the Silicon-Hydrogen Bond by Phosphorus Pentafluoride

1. Fluorination of Organosilanes

a. The Preparation and Properties of 3-Monofluorosilylpropene and 3-Difluorosilylpropene

(1) Preparation

Into a high pressure tube fitted with a teflon needle valve⁴² was condensed CH₂=CHCH₂SiH₃ (1.38 millimoles) and PF₅ (1.5 millimoles). The tube was immersed into a -45° temperature bath for 11 hours. After removal of hydrogen, the volatile products were distilled: R.T. → -116° → -196°. The -196° fraction consisted of various

fluorides of phosphorus and silicon, including PF_3 ,²⁰⁹ SiH_3F ,¹⁴⁰ SiH_2F_2 ,⁴⁶ and unreacted PF_5 ,¹⁴⁴ identified by their infrared spectra. The -116° fraction, containing fluorides of 3-silylpropene, was purified by gas chromatography (see below). The reaction yielded 74.8 mg. (60%) of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ and 7.5 mg. (6%) of $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$. An identical reaction performed at 0° for 5 hours resulted in a 20% yield of 3-monofluorosilylpropene.

(2) Gas Chromatography

The -116° fraction was purified using the gas chromatograph. Conditions used were: column A, column temperature = 28° , detector temperature = 75° , flow rate = 70.6 ml./min. The peaks collected and their retention times are listed in Table II-26.

Table II-26

Retention Times for the G. C. Separation of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$
and $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$ from Impurities

t_r (minutes)	Assignment
20.96	$\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$
22.73	$\text{CH}_2=\text{CHCH}_2\text{SiH}_3$
26.81	$\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$

(3) Gas Phase Molecular Weight

The gas phase molecular weight of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ was determined by the standard Dumas method and found to be 90.0 (calc. 90.12).

(4) Precise Mass Measurement

A precise mass measurement was performed on the "parent

minus one hydrogen" peak in the mass spectrum of each compound. The results are summarized in Table II-27.

Table II-27
Precise Mass Measurement Data for $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$
and $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$

Ion (empirical formula)	Measured Mass	Calculated Mass
$\text{C}_3\text{H}_7\text{SiF}$	90.0312	90.0301
$\text{C}_3\text{H}_6\text{SiF}_2$	108.0190	108.0206

(5) Melting Point

The melting point of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$, determined by the Stock method,¹⁸¹ was -137.0° .

(6) Vapor Pressure

A vapor pressure curve was determined for $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$. The glass manometer system had been pretreated with an impure sample of the compound for several hours. The data provided by a least squares computer analysis of the observed temperatures and pressures are listed in Tables II-28 and II-29 and Figure II-0.

(7) Thermal Stability

A sample of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ collected from the gas chromatograph at a retention time of 26.8 minutes was allowed to warm to room temperature for several minutes. A mass spectrum of this sample was obtained and found to contain "parent minus one hydrogen" peaks at 90, 108 and 126, corresponding to $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$, $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$ and $\text{CH}_2=\text{CHCH}_2\text{SiF}_3$, respectively. However, a sample taken directly from the

Table II-28
 Vapor Pressure of 3-Monofluorosilylpropene^a

Exptl. Press.	Temp. (°C)	Calc. Press.	Calc.Press.-Exptl.Press.
<u>Increasing Temperature</u>			
10.98	-57.4	10.65	-.33
13.86	-53.6	13.92	.06
17.50	-50.0	17.79	.29
20.01	-47.9	20.41	.40
21.37	-46.9	21.83	.46
24.80	-45.1	24.53	-.27
29.47	-42.2	29.47	.00
35.99	-39.0	35.80	-.19
36.94	-38.6	36.79	-.15
44.10	-35.7	43.77	-.33
46.84	-34.6	46.78	-.06
53.60	-32.3	53.46	-.14
<u>Decreasing Temperature</u>			
46.85	-34.7	46.50	-.35
40.65	-37.1	40.27	-.38
33.01	-40.4	33.02	.01
27.63	-43.5	27.16	-.47
24.95	-45.0	24.69	-.26
18.09	-50.1	17.67	-.42

^a All pressures given in millimeters of mercury.

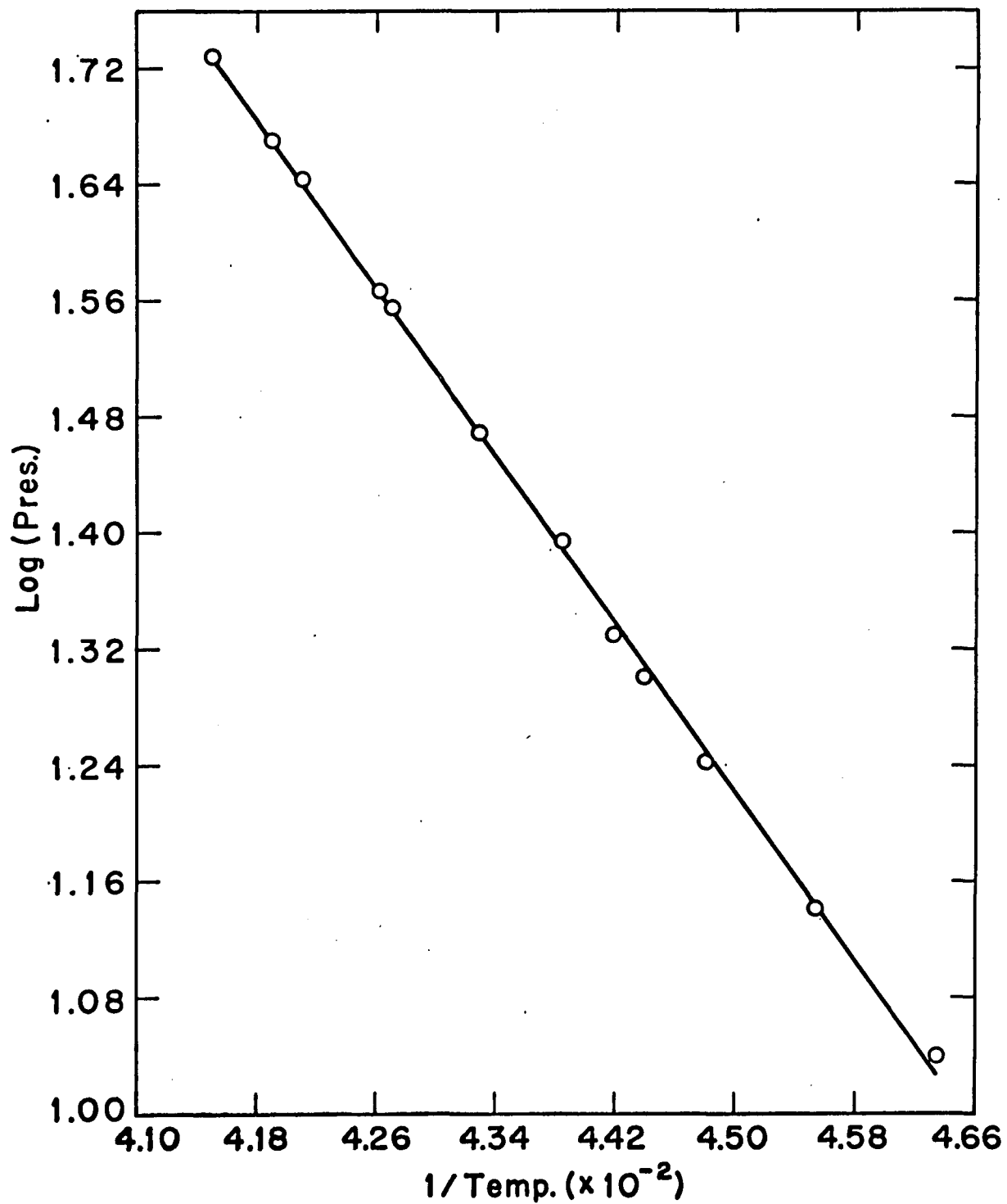


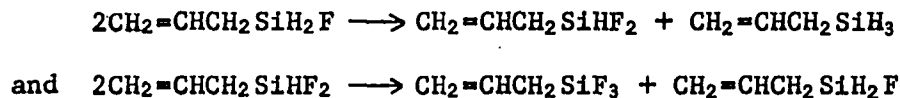
Figure II-0 - Vapor Pressure of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$

Table II-29

Data for $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ Derived from Vapor Pressure Plot

Slope = -1448.72	Heat of Vaporization = 6629.26 cal. mole ⁻¹
Intercept = 7.74203	Trouton's Constant = 22.24 cal. mole ⁻¹ deg. ⁻¹
Boiling Point = 24.86°C	Sum Square = .0701

gas chromatograph to the mass spectrometer with no appreciable warming period revealed a single "parent minus one hydrogen" peak at $m/e = 90$. Similar observations were noted for $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$, though a pure sample of this compound was unobtainable. These observations imply that the two compounds disproportionate readily at room temperature, probably via the reactions:



(8) Infrared Spectrum

The infrared spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ in the gas phase was recorded at pressures of 5 torr and 50 torr. The infrared spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$ in the gas phase was recorded at pressures of 5 torr and 25 torr. The spectra are shown in Figures II-P and II-Q, while the band assignments are listed in Tables II-30 and II-31.

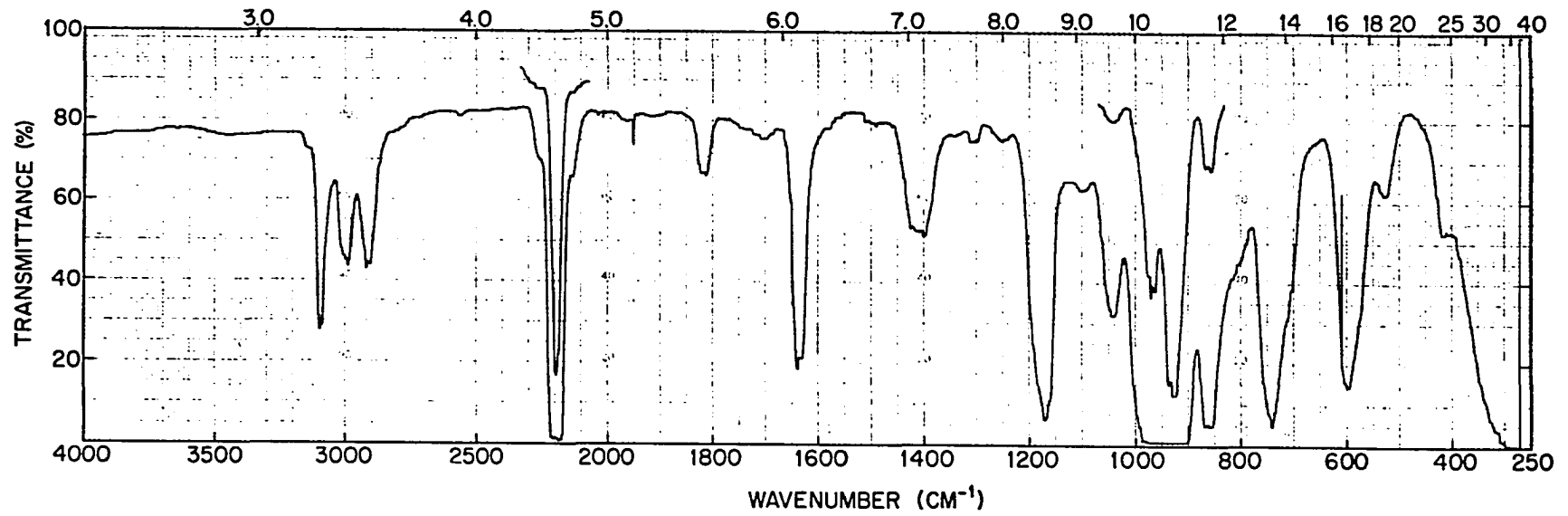


Figure II-P - Infrared Spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$

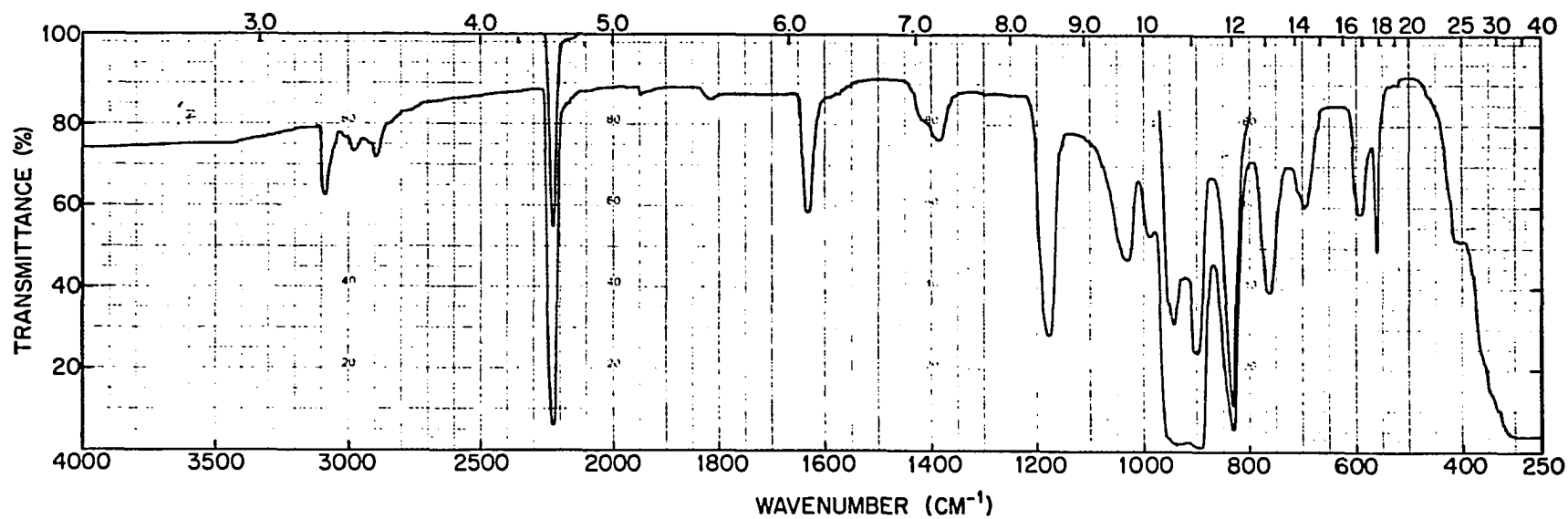


Figure II-Q - Infrared Spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$

Table II-30
Infrared Absorption Frequencies of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$

Absorption (cm^{-1})	Intensity ^a	Assignment ^a	Reference
3100 3095 3085	m	$\nu_a(\text{CH}_2=)$	11,74,94
2988	w	$\nu_s(\text{CH}_2=)$	94
2910 2904	w	$\nu_s(\text{CH}_2)$	74,94
2194	s	$\nu_s, \nu_a(\text{SiH}_2)$	63,140
1820 1813	w	$856 + 970 = 1826$	11,74
1639 1632	m	$\nu(\text{C}=\text{C})$	11,51,94
1436 1411 1399	w	$\delta(\text{CH}_2=)$ $\delta(\text{CH})$	11,74,94
1170	s	$t(\text{CH}_2)$	158,159
1042	s	$\nu(\text{C}-\text{C})$	74,131,158
975 970 962	vs	$\nu(\text{Si}-\text{F})$	37,140
936 927	vs	$\delta(\text{SiH}_2)$	131,140
868 856	s	$w(\text{SiH}_2)$	158
742	s	$t(\text{SiH}_2)$ $\rho(\text{CH}_2)$	46,63,158
599	m	$\nu(\text{Si}-\text{C})$	73,175
527	vw	$\rho(\text{SiH}_2)$	158
417	w	$\delta(\text{C}=\text{C}-\text{C})$	94

^a For explanation of symbols, see Appendix.

Table II-31

Infrared Absorption Frequencies of $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$

Absorption (cm^{-1})	Intensity ^a	Assignment ^a	Reference
3085	m	$\nu_a(\text{CH}_2=)$	11,74,94
2980	w	$\nu_s(\text{CH}_2=)$	94
2895	w	$\nu_s(\text{CH}_2)$	74,94
2230	s	$\nu_a, \nu_s(\text{SiH})$	46,63
1825	vw	$845 + 973 = 1818$	
1633	m	$\nu(\text{C}=\text{C})$	11,51,94
1387	w	$\delta(\text{CH}_2=), \delta(\text{CH})$	11,74,94
1178	s	$\tau(\text{CH})$	158,159
1130	m	$\nu(\text{C}-\text{C})$	74,131,158
973	m	$\nu_a(\text{Si}-\text{F})$	46
955 945	vs	$\delta(\text{SiH})$	131,140
907 900	vs	$\nu_s(\text{Si}-\text{F})$	46
845	s	$w(\text{SiH})$	158
766	ms	$\rho(\text{CH}_2)$	131,157
695	m	unassigned	
593	m	$\nu(\text{Si}-\text{C})$	73,175
550	m	$\rho(\text{SiH})$	158
414 404	m	$\delta(\text{C}=\text{C}-\text{C})$	94

^a For explanation of symbols, see Appendix.

(9) Proton Magnetic Resonance Spectrum

The proton magnetic resonance spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ was obtained from a 10 v/v% sample in deuteriochloroform. Approximately 2% of tetramethylsilane was added as an internal reference. Figures II-R and II-S are spectra recorded on the 60 MHz. and 250 MHz. spectrometers at a sweep width of 600 Hz. and 1500 Hz., respectively. An expanded spectrum may be found in section II.G. and further discussion in section III.C.

(10) Mass Spectrum

A mass spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ was obtained at an ionizing voltage of 70 electron volts. The resulting fragmentation is listed in Table II-32. The mass spectrum of a pure sample of $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$ proved impossible to achieve.

Table II-32

Mass Spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$

m/e	Relative Intensity (%)	Assignment	m/e	Relative Intensity (%)	Assignment
92	3.6	$\text{C}_3\text{H}_7^{30}\text{SiF}$	48	11.8	SiHF
91	8.3	$\text{C}_3\text{H}_7^{29}\text{SiF}$	47	100.0	SiF
90	51.6	$\text{C}_3\text{H}_7\text{SiF}$	44	37.0	CH_4Si
89	33.9	$\text{C}_3\text{H}_6\text{SiF}$	43	9.0	CH_3Si
88	9.4	$\text{C}_3\text{H}_5\text{SiF}$	42	10.8	CH_2Si
76	3.3	$\text{C}_2\text{H}_4^{29}\text{SiF}$	41	37.9	$\text{CHSi}, \text{C}_3\text{H}_5$
75	22.6	$\text{C}_2\text{H}_4\text{SiF}$	40	7.2	$\text{CSi}, \text{C}_3\text{H}_4$
64	5.7	CH_5SiF	39	34.1	C_3H_3
63	24.3	CH_4SiF	29	2.3	SiH
62	84.2	CH_3SiF	28	14.8	Si
49	36.9	SiH_2F			

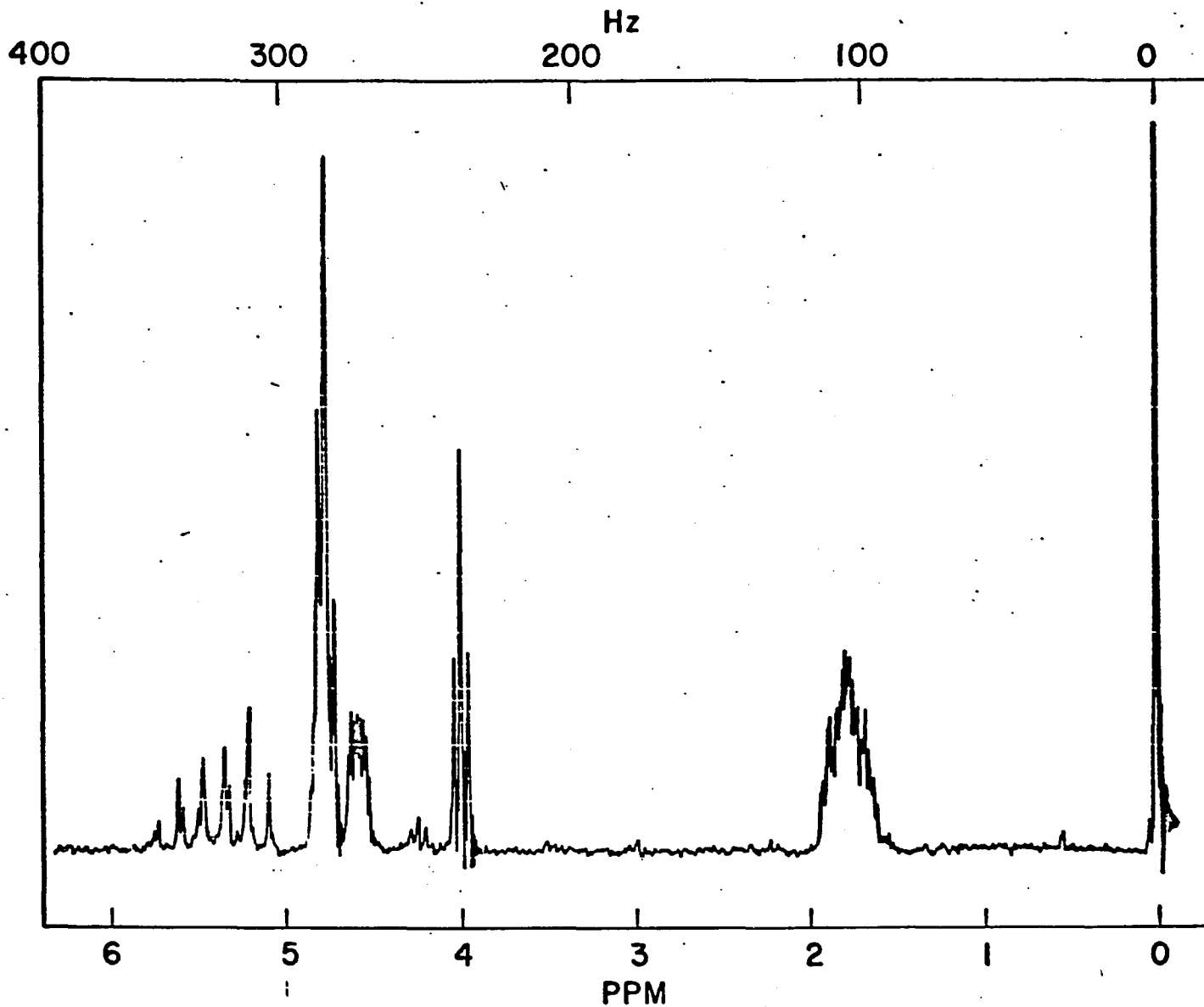


Figure II-R - Proton Magnetic Resonance Spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ at 60 Hz. Sweep Width (60 MHz.)

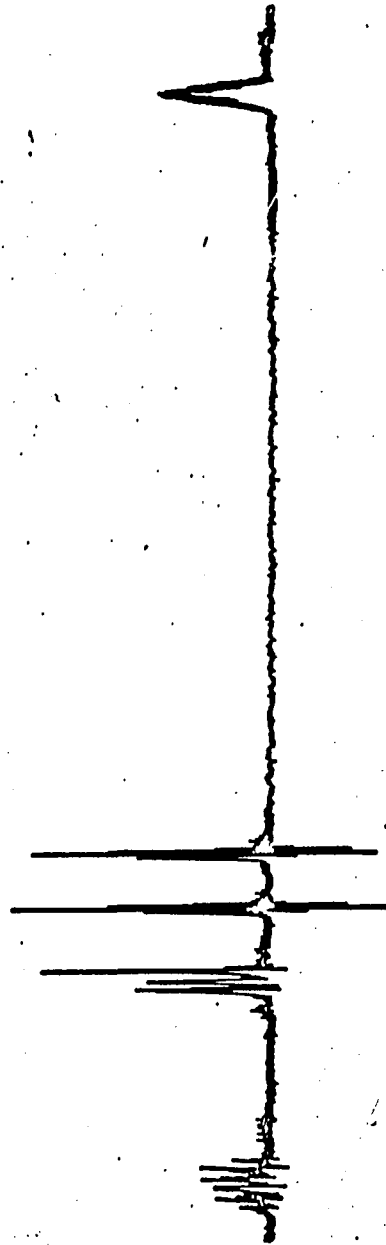


Figure II-S - Proton Magnetic Resonance Spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$
at 1500 Hz. Sweep Width (250 MHz.)

2. Fluorination of Silylamines

a. The Formation of Fluorosilylamines by the Interaction of Phosphorus Pentafluoride with Trisilylamine

(1) Procedure

Trisilylamine (110.7 mg., 1.03 millimoles) and phosphorus pentafluoride (3.1 millimoles) were condensed into a break-seal tube and maintained at 0° for 20 minutes. No noncondensable gas was detected upon opening the tube. The volatile products were distilled: R.T. → -96° → -196°. An infrared spectrum of the -196° fraction identified its constituents as PF₃,²⁰⁹ SiH₃F,¹⁴⁰ SiH₂F₂,⁴⁶ and unreacted PF₅.¹⁴⁴ A mass spectrum of the -96° fraction yielded peaks which were readily assignable to mono-, di-, and trifluorotrisilylamine.

A similar reaction with a 6-fold excess of PF₅ [7.56 millimoles of PF₅ and 134.5 mg., 1.26 millimoles of (SiH₃)₃N] was allowed to proceed at -23° for 20 minutes and the volatile products were distilled as above. Mass spectral evidence revealed the -96° fraction as containing SiH₃N(SiH₂F)₂ as the major component with a smaller quantity of (SiH₃)₂NSiH₂F also present.

A number of similar reactions with varying conditions were carried out for the preparation of the various trisilylamines. However, in most cases SiH₃N(SiH₂F)₂ was the major product. The volatile components from several reactions were combined and adequate separation was achieved on the low-pressure fractionating column (Figure II-B). Of the three fluoro compounds obtained from this separation, only the difluoro was characterized fully. The other two were characterized as fully as quantities permitted.

(2) Gas Phase Molecular Weight of 1,1'-Difluorotrisilylamine

The molecular weight of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$ was determined by the standard Dumas method and found to be 143.3 (calc. 144.40).

(3) Melting Point of 1,1'-Difluorotrisilylamine

The melting point of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$, determined by the Stock method,¹⁸¹ was -89.7° .

(4) Vapor Pressure of 1,1'-Difluorotrisilylamine

The vapor pressure of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$ was determined at various temperatures in the range -46° to -16° in a mercury manometer system, the glass walls of which had been pretreated for ~ 16 hours with an impure sample of the compound. The data derived from a least squares computer analysis of the experimental pressures and temperatures is summarized in Tables II-33 and II-34 and Figure II-T.

(5) Infrared Spectra of 1,1'-Difluorotrisilylamine

The infrared spectrum of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$ was recorded in the gas phase at pressures of 5 torr and 20 torr. The spectrum is shown in Figure II-U and the band assignments are given in Table II-35.

Table II-33
Vapor Pressure of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$

Exptl. Press.	Temp. ($^{\circ}\text{C}$)	Calc. Press.	Calc.Press.-Exptl.Press.
<u>Increasing Temperature</u>			
7.72	-46.0	7.72	.00
8.41	-45.0	8.36	-.05
14.02	-37.8	14.29	.27
23.31	-30.8	23.31	-.00
27.63	-28.6	27.02	-.61
30.44	-26.8	30.38	-.06
34.23	-25.0	34.12	-.11
38.94	-22.9	39.12	.18
44.81	-20.7	44.81	.00
52.91	-18.0	53.03	.12
57.23	-16.6	57.57	.34
<u>Decreasing Temperature</u>			
44.97	-21.7	42.05	-2.92
28.38	-31.0	22.90	-5.48
20.74	-36.9	15.19	-5.55

^a All pressures given in millimeters of mercury.

Table II-34
Data for $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$ Derived from Vapor Pressure Plot

Slope = -1731.88	Heat of Vaporization = 7926.00 cal. mole ⁻¹
Intercept = 8.5119	Trouton's Constant = 25.77 cal. mole ⁻¹ deg. ⁻¹
Boiling Point = 34.39 $^{\circ}\text{C}$	Sum Square = .0556

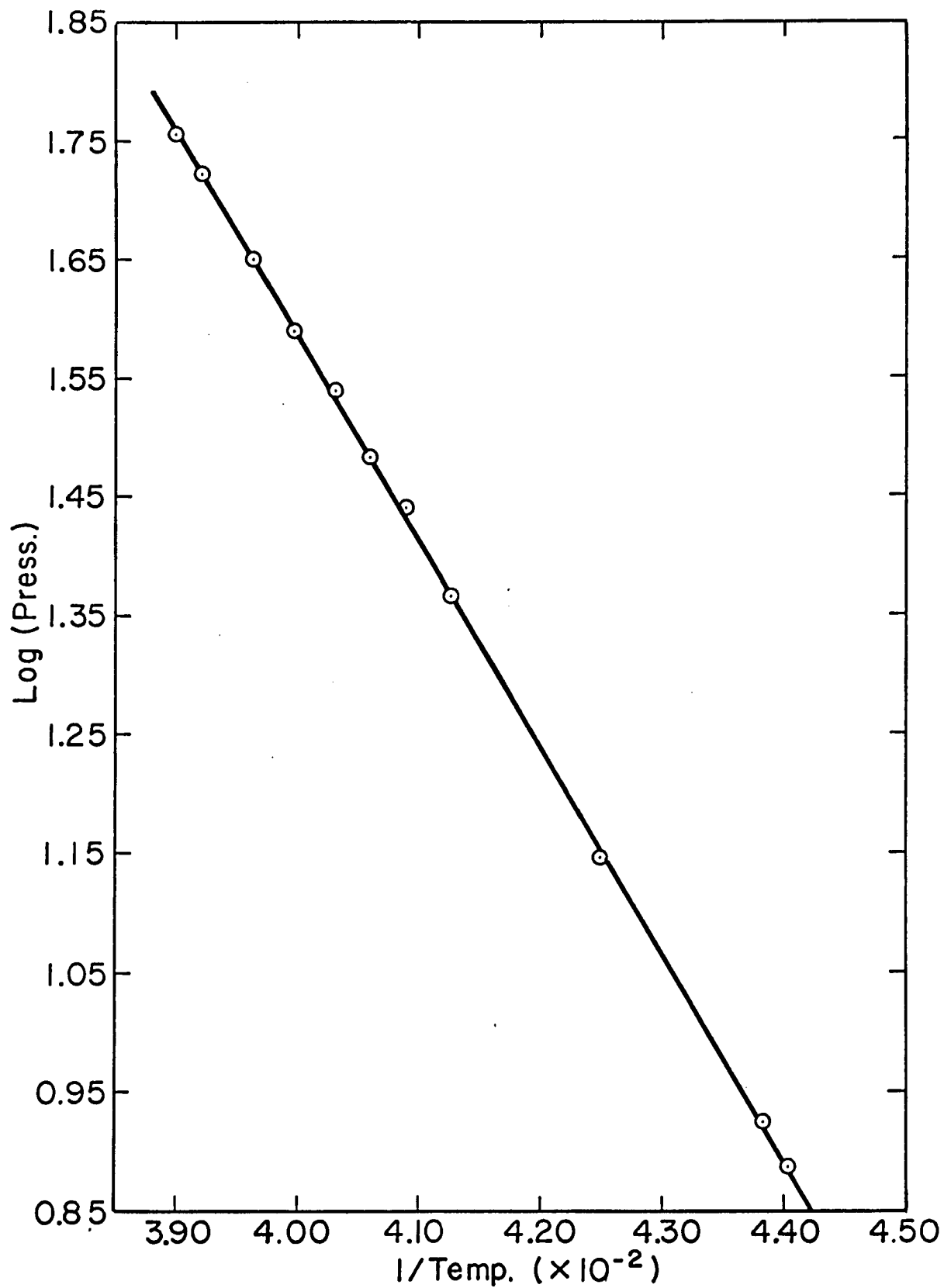


Figure II-T - Vapor Pressure of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$

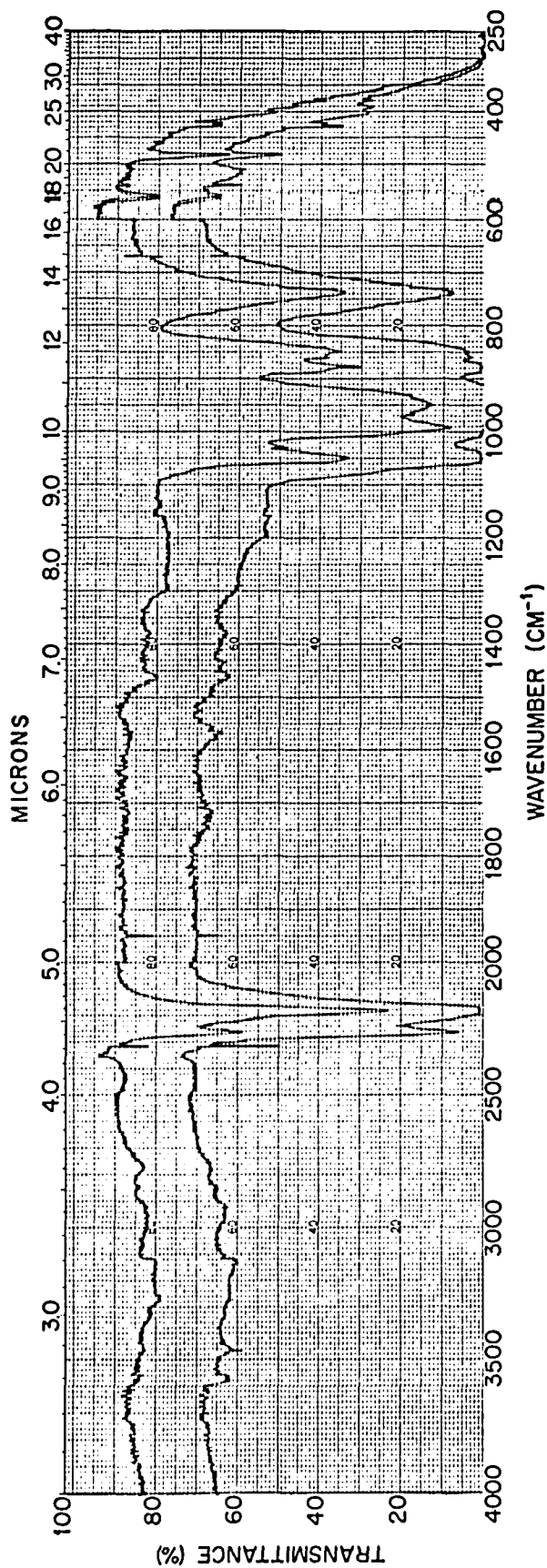
Figure II-U - Infrared Spectrum of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$

Table II-35

Infrared Absorption Frequencies for $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$

Absorption (cm^{-1})	Intensity ^a	Assignment ^a	Reference
3575	w	$2 \times 849 + 2 \times 950 = 3598$	
3468	w	$2 \times 738 + 2 \times 992 = 3456$	
3316	mw	$1050 + 2264 = 3314$	
2264	s	$\nu_a, \nu_s(\text{SiH}_2)$	46
2182	vs	$\nu_a, \nu_s(\text{SiH}_3)$	61,131,155
1568	w	$849 + 738 = 1587$	
1050	s	$\nu_a(\text{Si-N})$	61,155,203
992	vs	$\delta(\text{SiH}_2)$	38,39
950	vs	$\delta(\text{SiH}_3)$	38,62
878	s	$\nu(\text{Si-F})$	46,140,203
849	s	$w(\text{SiH}_2), w(\text{SiH}_3)$	158
738	s	$\rho(\text{SiH}_2), \rho(\text{SiH}_3)$	39,61,62,155
560	w	Impurity	
540	w	$\nu_s(\text{Si}_3\text{N})$	203
518 510	w	unassigned	
482	w	Impurity	
428 422	w	unassigned	
402 392	w	$\delta(\text{Si}_3\text{N})$	86

^a For explanation of symbols, see Appendix.

(6) Precise Mass Measurement Data for the Three Fluoro-trisilylamines

The "parent minus one hydrogen" peak of the mass spectrum of each fluoro compound was precisely mass measured. The results are presented in Table II-36.

Table II-36

Precise Mass Measurement Data for Fluorotrisilylamines

Ion (empirical formula)	Measured Mass	Calculated Mass
$\text{Si}_3\text{H}_7\text{FN}$	123.9870	123.9886
$\text{Si}_3\text{H}_6\text{F}_2\text{N}$	141.9776	141.9782
$\text{Si}_3\text{H}_5\text{F}_3\text{N}$	159.9682	159.9674

(7) Thermal Stability of the Three Fluorotrisilylamines

A sample of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$ was condensed into a break-seal tube and allowed to warm to room temperature. The sample at this temperature was entirely in the gas phase. The infrared spectrum of the sample after two days was unchanged. A light gray ring observed around the inside of the tube was concluded to have originated from slight decomposition of the product as it passed through the liquid state. Further evidence for the compound's instability in the liquid phase is obtained from noticing the marked differences between experimental and calculated pressures during the decreasing temperature portion of the vapor pressure measurement.

$(\text{SiH}_2\text{F})_3\text{N}$ decomposed quite readily, including during purification through the low-pressure fractionating column.

$(\text{SiH}_3)_2\text{NSiH}_2\text{F}$ was unobtainable in sufficient quantities to permit determination of its thermal stability.

(8) Proton Magnetic Resonance Spectra for the Three Fluorotrisilylamines

The proton magnetic resonance spectra of reasonably pure samples of $(\text{SiH}_2\text{F})_3\text{N}$ and $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$ were determined at concentrations of 6 v/v% in cyclopentane. In the spectrum for the former compound, the SiH_2 protons are split by the adjacent fluorines, giving rise to a doublet centered at 5.15τ . The spectrum for the latter compound is composed of a doublet and a triplet. The doublet (at 5.20τ) arises, as in the trifluorotrisilylamine spectrum, from the splitting of the SiH_2 protons by the adjacent fluorines. The triplet (at 5.59τ) is due to the long range splitting of the SiH_3 protons by the fluorines on the two SiH_2F groups. The spectra for these two compounds are shown in Figure II-V and the pmr data for the fluorotrisilylamines are presented in Table II-37.

Table II-37

Proton Magnetic Resonance Data for Fluorotrisilylamines

Compound	SiH_3 Chemical Shift ^a	SiH_2 Chemical Shift ^a	J_{HF} (adjacent) ^b	J_{HF} (long range) ^b
$(\text{SiH}_3)_2\text{NSiH}_2\text{F}$	d	5.27^c	60.3^c	d
$\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$	5.59	5.20	60.3	1.52
$(\text{SiH}_2\text{F})_3\text{N}$	--	5.15	60.3	d

^a Values reported according to the τ scale.

^b Values reported in Hz.

^c Values obtained as described on page 167.

^d Not observed.

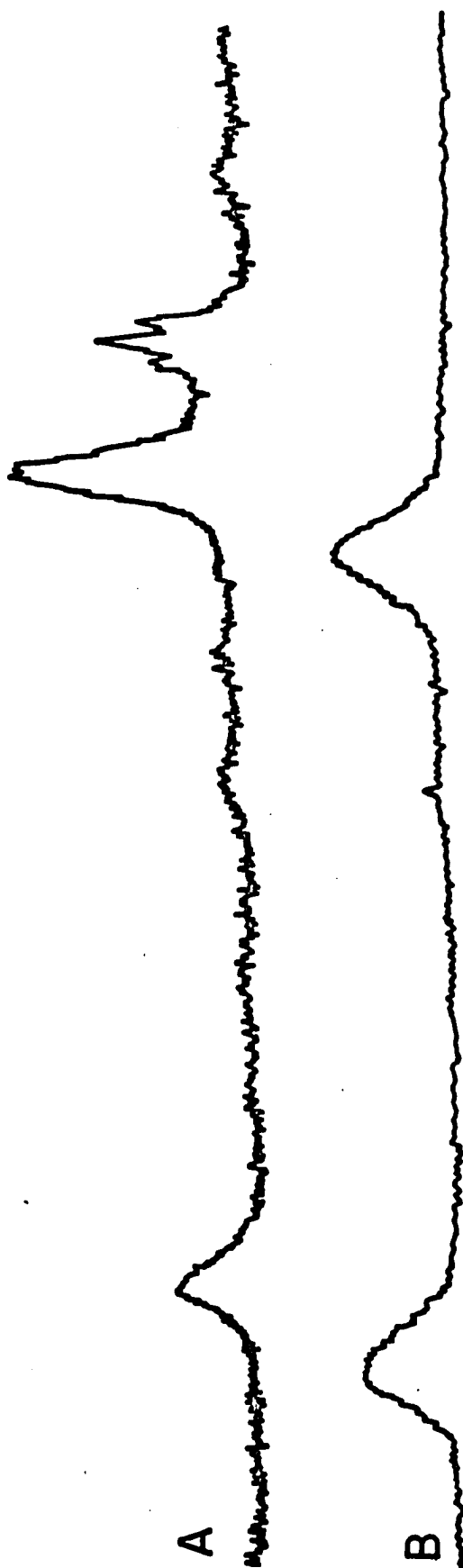


Figure II-V - Proton Magnetic Resonance Spectra of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$ (A) and $(\text{SiH}_2\text{F})_3\text{N}$ (B) at 250 Hz. Sweep Width (100 MHz.)

Table II-38

Mass Spectrum of $(\text{SiH}_3)_2\text{NSiH}_2\text{F}$

m/e	Relative Intensity (%)	Assignment	m/e	Relative Intensity (%)	Assignment
127	4.0	$^{30}\text{SiSi}_2\text{H}_8\text{FN}$	90	29.1	Si_2HFN
126	15.7	$^{29}\text{SiSi}_2\text{H}_8\text{FN}$	77	3.0	$^{30}\text{SiSiH}_5\text{N}$
125	53.0	$\text{Si}_3\text{H}_8\text{FN}$	76	7.6	$^{29}\text{SiSiH}_5\text{N}$
124	100.0	$\text{Si}_3\text{H}_7\text{FN}$	75	10.0	$\text{Si}_2\text{H}_5\text{N}$
123	40.9	$\text{Si}_3\text{H}_6\text{FN}$	74	77.4	$\text{Si}_2\text{H}_4\text{N}$
122	29.6	$\text{Si}_3\text{H}_5\text{FN}$	73	7.4	$\text{Si}_2\text{H}_3\text{N}$
121	37.4	$\text{Si}_3\text{H}_4\text{FN}$	72	53.0	$\text{Si}_2\text{H}_2\text{N}$
96	3.7	$^{30}\text{SiSiH}_5\text{FN}$	71	21.7	Si_2HN
95	8.2	$^{29}\text{SiSiH}_5\text{FN}$	70	38.3	Si_2N
94	11.5	$\text{Si}_2\text{H}_5\text{FN}$	50	3.9	$^{29}\text{SiH}_3\text{F}$
93	8.2	$\text{Si}_2\text{H}_4\text{FN}$	49	28.3	SiH_3F
92	35.2	$\text{Si}_2\text{H}_3\text{FN}$	48	15.6	SiH_2F
91	11.2	$\text{Si}_2\text{H}_2\text{FN}$	47	17.8	SiHF

(9) Mass Spectra for the Three Fluorotrisilylamines

The mass spectra of the three fluorotrisilylamines were determined at an ionizing voltage of 70 electron volts. The resulting data are listed in Tables II-38, II-39, and II-40.

Table II-39
Mass Spectrum of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$

m/e	Relative Intensity (%)	Assignment	m/e	Relative Intensity (%)	Assignment
145	1.0	$^{30}\text{SiSi}_2\text{H}_7\text{F}_2\text{N}$	90	13.2	Si_2HFN
144	3.1	$^{29}\text{SiSi}_2\text{H}_7\text{F}_2\text{N}$	77	3.1	$^{30}\text{SiSiH}_5\text{N}$
143	8.1	$\text{Si}_3\text{H}_7\text{F}_2\text{N}$	76	2.5	$^{29}\text{SiSiH}_5\text{N}$
142	21.5	$\text{Si}_3\text{H}_6\text{F}_2\text{N}$	75	3.0	$\text{Si}_2\text{H}_5\text{N}$
141	9.4	$\text{Si}_3\text{H}_5\text{F}_2\text{N}$	74	13.1	$\text{Si}_2\text{H}_4\text{N}$
140	7.4	$\text{Si}_3\text{H}_4\text{F}_2\text{N}$	73	3.1	$\text{Si}_2\text{H}_3\text{N}$
139	7.5	$\text{Si}_3\text{H}_3\text{F}_2\text{N}$	72	10.6	$\text{Si}_2\text{H}_2\text{N}$
113	3.8	--	71	1.2	Si_2HN
112	3.1	$\text{Si}_2\text{H}_4\text{F}_2\text{N}$	70	5.9	Si_2N
111	4.1	$\text{Si}_2\text{H}_3\text{F}_2\text{N}$	51	3.9	$^{30}\text{SiH}_2\text{F}$
110	4.1	$\text{Si}_2\text{H}_2\text{F}_2\text{N}$	50	8.3	$^{29}\text{SiH}_2\text{F}$
93	4.9	$\text{Si}_2\text{H}_4\text{FN}$	49	100.0	SiH_2F
92	21.1	$\text{Si}_2\text{H}_3\text{FN}$	48	58.4	SiHF
91	3.4	$\text{Si}_2\text{H}_2\text{FN}$	47	32.0	SiF

Table II-40
Mass Spectrum of $(\text{SiH}_2\text{F})_3\text{N}$

m/e	Relative Intensity (%)	Assignment	m/e	Relative Intensity (%)	Assignment
162	3.3	$^3\text{SiSi}_2\text{H}_5\text{F}_3\text{N}$	93	6.0	$\text{Si}_2\text{H}_4\text{FN}$
161	6.3	$^2\text{SiSi}_2\text{H}_5\text{F}_3\text{N}$	92	23.7	$\text{Si}_2\text{H}_3\text{FN}$
160	24.9	$\text{Si}_3\text{H}_5\text{F}_3\text{N}$	91	5.6	$\text{Si}_2\text{H}_2\text{FN}$
159	11.1	$\text{Si}_3\text{H}_4\text{F}_3\text{N}$	90	17.9	Si_2HFN
158	8.2	$\text{Si}_3\text{H}_3\text{F}_3\text{N}$	51	4.6	$^3\text{SiH}_2\text{F}$
157	6.4	$\text{Si}_3\text{H}_2\text{F}_3\text{N}$	50	13.5	$^2\text{SiH}_2\text{F}$
113	7.0	---	49	100.0	SiH_2F
112	5.9	$\text{Si}_2\text{H}_4\text{F}_2\text{N}$	48	35.1	SiHF
111	8.4	$\text{Si}_2\text{H}_3\text{F}_2\text{N}$	47	43.6	SiF
110	13.5	$\text{Si}_2\text{H}_2\text{F}_2\text{N}$			

b. The Reaction of Phosphorus Pentafluoride with 1,1,1',1'-Tetramethyldisilylamine

Summary: PF_5 and $[(\text{CH}_3)_2\text{SiH}]_2\text{NH}$ in a 1:1 ratio reacted at -45° and -78° to yield $(\text{CH}_3)_2\text{SiHF}$, $(\text{CH}_3)_2\text{SiF}_2$, PF_3 . $(\text{CH}_3)_2\text{SiFNHSiH}(\text{CH}_3)_2$ was most likely formed, but appeared to be thermally unstable, decomposing to yield $(\text{CH}_3)_2\text{SiF}_2$ plus other cleavage products.

Experiment A: Equimolar portions (1.2 millimoles) of PF_5 and $[(\text{CH}_3)_2\text{SiH}]_2\text{NH}$ were condensed into a reaction tube sealed by a teflon needle valve.⁴² The tube was allowed to warm to -45° for 15 minutes, after which the volatile products were distilled: R.T. $\rightarrow -64^\circ \rightarrow -196^\circ$. Infrared and mass spectrometric identification indicated that the -196°

fraction consisted of PF_3 ,²⁰⁹ unreacted PF_5 ,¹⁴⁴ and the cleavage products $(\text{CH}_3)_2\text{SiHF}$ and $(\text{CH}_3)_2\text{SiF}_2$,¹⁷⁹ while the -64° fraction contained the starting material, $[(\text{CH}_3)_2\text{SiH}]_2\text{NH}$.¹²¹

Experiment B: PF_5 (.7 millimoles) and $[(\text{CH}_3)_2\text{SiH}]_2\text{NH}$ (.77 millimoles) were condensed into a reaction tube sealed by a teflon needle valve.⁴² The tube was immersed in a -78° temperature bath for 10 minutes, after which a large amount of hydrogen was removed and the volatile products distilled: R.T. $\longrightarrow -64^\circ \longrightarrow -196^\circ$. The -196° fraction contained PF_3 ,²⁰⁹ unreacted PF_5 ,¹⁴⁴ and the cleavage products $(\text{CH}_3)_2\text{SiHF}$ and $(\text{CH}_3)_2\text{SiF}_2$ ¹⁷⁹ as evidenced by their infrared spectra, while the -64° fraction consisted of only the starting amine.¹²¹

The presence of $(\text{CH}_3)_2\text{SiF}_2$ in the reaction products indicates that the monofluoroamine has probably formed and immediately undergone cleavage by PF_5 .

3. Fluorination of Organosilicon Ethers

a. The Reaction of Phosphorus Pentafluoride with 1,1,1',1'-Tetramethyldisiloxane

Summary: PF_5 and $[(\text{CH}_3)_2\text{SiH}]_2\text{O}$ in a 2:1 ratio reacted at -78° to give $[(\text{CH}_3)_2\text{SiF}]_2\text{O}$, PF_3 , POF_3 , $(\text{CH}_3)_2\text{SiHF}$ and $(\text{CH}_3)_2\text{SiF}_2$. PF_5 and $[(\text{CH}_3)_2\text{SiH}]_2\text{O}$ in a 1:1 ratio underwent reaction at -96° to give $(\text{CH}_3)_2\text{SiHF}$, $(\text{CH}_3)_2\text{SiF}_2$, PF_3 , POF_3 , $(\text{CH}_3)_2\text{SiFOSiH}(\text{CH}_3)_2$ and $[(\text{CH}_3)_2\text{SiF}]_2\text{O}$. In each reaction, higher temperatures and/or significantly longer reaction times produced exclusively cleavage products and various fluorides of phosphorus.

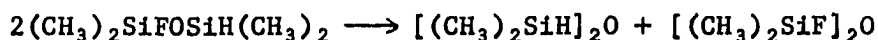
Experiment A: Symmetrical tetramethyldisiloxane (305 mg., 2.3 millimoles) and phosphorus pentafluoride (5.1 millimoles) were condensed into a breakseal tube and warmed to -78° for 20 minutes. No

noncondensable gas was detected and the volatile products were distilled: R.T. \longrightarrow -78° \longrightarrow -196°. The infrared spectrum of the -78° fraction was identical to the published spectrum⁷¹ of 1,1'-difluoro-1,1,1',1'-tetramethyldisiloxane. Infrared evidence also indicated that the -196° fraction contained PF₃,²⁰⁹ POF₃,⁹⁵ unreacted PF₅,¹⁴⁴ and the cleavage products (CH₃)₂SiHF and (CH₃)₂SiF₂.¹⁷⁹ The purity of the -78° fraction was substantiated by a Dumas gas phase molecular weight determination (found 170.0, calc. 170.31) and by mass spectrometry. Total yield of product was >50%.

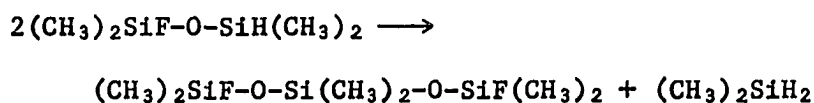
1,1'-Difluoro-1,1,1',1'-tetramethyldisiloxane has been previously prepared by the hydrolysis of (CH₃)₂SiFBr with water in ether⁷¹ and by the thermal disproportionation of tris(dimethylfluorosiloxy)borane.¹³³ The method of Kifer and Van Dyke,¹¹⁶ i.e., fluorination by phosphorus pentafluoride, seems preferable to previous methods of preparation for this compound due to the simplicity of the method and the ease of reaction.

Experiment B: Symmetrical tetramethyldisiloxane (269 mg., 2.0 millimoles) and PF₅ (2.1 millimoles) were condensed into a breakseal tube and permitted to react at -96° for 4 minutes. No noncondensable gas was detected and the volatile products were distilled: R.T. \longrightarrow -96° \longrightarrow -196°. Infrared evidence indicated that the -196° fraction contained PF₃,²⁰⁹ POF₃,⁹⁵ unreacted PF₅,¹⁴⁴ and the cleavage products (CH₃)₂SiHF and (CH₃)₂SiF₂.¹⁷⁹ The two uppermost peaks revealed in a mass spectrum of the -96° fraction had a m/e of 151 and 155. The peak having m/e of 151 is assignable to the ion [(CH₃)₂SiOSiF(CH₃)₂]⁺ and the 155 peak is assignable to the ion [(CH₃)₂SiFOSiF(CH₃)₂]⁺. The 155 ion is unambiguously assignable to the parent [(CH₃)₂SiF]₂O minus a methyl group. The peak

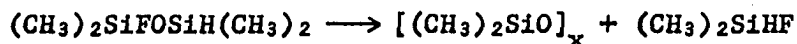
at $m/e = 151$ can arise from either the "parent minus one hydrogen" ion of the monofluoro compound, or from the loss of fluorine from the difluoro compound. To determine which alternative was correct, a mass spectrum of a pure sample of $[(CH_3)_2SiF]_2O$ was obtained. The spectrum contained no peaks in the m/e region of 151. This evidence plus the fact that a gas chromatographic separation of a typical 1:1 reaction yielded solely $[(CH_3)_2SiF]_2O$ (column D, column temperature = 31° , detector temperature = 85° , flow rate = 100 ml./min., $t_r = 26.60$ minutes) indicates that 1-monofluoro-1,1,1',1'-tetramethyldisiloxane has been formed, but once formed, is thermally unstable. A disproportionation reaction such as the following might have occurred:



Successive gas phase molecular weight determinations manifested a continual decrease. A solid, white material was visible on the walls of the vacuum line cold finger. The evidence here yields a conclusion of a decomposition process producing a solid of unknown composition but of relatively high molecular weight plus gases of lower molecular weight, such as $(CH_3)_2SiH_2$. One such reaction might be:



Another possible reaction is the elimination of $(CH_3)_2SiHF$:



F. The Attempted Preparation of Silylmethyl Cyanide and Silylmethyl Thiocyanate

1. The Reaction of Sodium Cyanide with Iodomethylsilane

Summary: NaCN was allowed to interact with $\text{SiH}_3\text{CH}_2\text{I}$ at room temperature both in the solid-gas phase and in the liquid-gas phase. No silicon hydride with a C-N bond was observed.

Experiment A: Glass wool was placed at the bottom of a glass column, on top of which was packed ~8 inches of NaCN. Glass wool was then packed on the cyanide. $\text{SiH}_3\text{CH}_2\text{I}$ (6.0 millimoles) was allowed to pass several times through the column. No noncondensable gas was produced and the infrared spectrum was unchanged.

The iodide was then expanded into the column and allowed to remain at room temperature for 1.5 hours. No noncondensable gas was produced and the volatile products were distilled: R.T. \longrightarrow -64° \longrightarrow -196° . The -64° fraction was shown by its infrared spectrum to consist of $\text{SiH}_3\text{CH}_2\text{I}$.⁶³ The -196° fraction had an infrared spectrum containing an Si-H stretching frequency and a mass spectrum was taken of the fraction. A precise mass measurement of the peak with the greatest m/e value indicated an ether of the type $(\text{CH}_3\text{SiH}_2)_2\text{O}$ (calc. 105.0192, meas. 105.0168). The difference between the measured and calculated values is large, but a computer program which predicts possible combinations of elements for a given measured mass indicated that the calculated mass for $\text{C}_2\text{H}_{10}\text{OSi}_2$ was the closest to the mass value obtained from the precise mass measurement. Also in the mass spectrum was a peak at m/e of 89, corresponding to the "parent minus one hydrogen" ion of $\text{SiH}_3\text{CH}_2\text{CH}_2\text{SiH}_3$.

Experiment B: Excess NaCN (3.2 millimoles) was dissolved in approximately 10 ml. of degassed acetone in a reaction flask. $\text{SiH}_3\text{CH}_2\text{I}$

(1 millimole) was condensed into the flask and allowed to interact with the cyanide at room temperature for one hour. After a considerable amount of hydrogen was removed, the volatile products were distilled: R.T. \longrightarrow -78° \longrightarrow -196° . The -196° fraction was identified by its infrared spectrum as SiH_3CH_3 ,¹³ while the -78° fraction contained acetone and some iodomethylsilane.⁶³

2. The Reaction of Silver Cyanide with Iodomethylsilane

Summary: AgCN was allowed to interact with $\text{SiH}_3\text{CH}_2\text{I}$ in a solid-gas phase reaction. No silicon hydride with a C-N bond was detected.

Experiment A: Glass wool was placed at the bottom of a glass column wrapped in aluminum foil which was then packed with AgCN . A wad of glass wool was packed on top of the cyanide to maintain it in place. $\text{SiH}_3\text{CH}_2\text{I}$ (1 millimole) was allowed to pass through the column several times. A small amount of hydrogen was removed after which the volatile products were distilled: R.T. \longrightarrow -64° \longrightarrow -196° . The -196° fraction consisted of SiH_3CH_3 ¹³ and HCN ¹⁶³ plus a small amount of acetone, occurring as an impurity from the iodomethylsilane preparation. The -64° fraction was not identified, but its infrared spectrum contained no Si-H stretching frequency.

3. The Reaction of Sodium Cyanide with Chloromethylsilane

Summary: NaCN was allowed to interact with $\text{SiH}_3\text{CH}_2\text{Cl}$ in DMSO below 20° . The products were SiH_4 , CH_3CN and SiH_3CH_3 . No evidence for a silicon hydride with a C-N bond was detected.

Experiment A: Sodium cyanide (0.3 g., 6 millimoles) was placed in a 100-ml. 3-neck round bottom flask. The flask was fitted with a dropping funnel, connected to the vacuum line and evacuated for several hours while being heated to 80° . Approximately 5 ml. of dimethylsulfoxide

(DMSO) was added by means of the dropping funnel. The DMSO was degassed and cooled to 12°. The NaCN-DMSO slurry was stirred and SiH₃CH₂Cl (0.7 millimoles) permitted to expand into the flask, remaining for 2 hours at a temperature maintained below 20°. Bubbling occurred during the reaction. Noncondensable material, presumably hydrogen, was removed and the volatile products distilled: R.T. → -116° → -196°. Infrared spectra showed the -196° fraction to consist of SiH₃CH₃¹³ (0.35 millimoles) and some SiH₄. The -116° fraction was further distilled: R.T. → -64° → -196°. The -196° fraction was identified by mass spectrometry as CH₃CN and a trace of (CH₃)₂S, while infrared spectra showed that the -64° fraction contained the starting chloride.⁶³

4. The Reaction of Iodomethylsilane with Sodium Cyanide and Silver Cyanide

Summary: SiH₃CH₂I was reacted with a mixture of NaCN and AgCN in the gas-solid phase. The product formed was SiH₃CH₃. No evidence of a silicon hydride containing a C-N bond was observed.

Experiment A: SiH₃CH₂I (10 millimoles) was condensed into a reaction flask containing NaCN (16 millimoles) and AgCN (12 millimoles). The iodide contained acetone as an impurity. The flask was immersed in a -78° temperature bath for 18 hours. Hydrogen was removed and the volatile products were distilled: R.T. → -116° → -196°. The -196° fraction had an infrared spectrum identical with that of SiH₃CH₃.¹³ The -116° fraction was shown to be the starting iodide⁶³ plus the acetone impurity.

5. The Reaction of Ammonium Thiocyanate with Iodomethylsilane

Summary: SiH₃CH₂I was allowed to interact with excess NH₄CNS at 38°. The product formed was SiH₃CH₃. No silicon hydride with a C-N bond was detected.

Experiment A: Ammonium thiocyanate (10 millimoles) was placed in a 250-ml. reaction flask and dried by evacuating the flask for an hour. Degassed acetone and $\text{SiH}_3\text{CH}_2\text{I}$ (6 millimoles) were condensed into the flask and refluxed gently at $\sim 38^\circ$. The hydrogen formed was removed and the volatile products distilled: $\text{R.T.} \rightarrow -116^\circ \rightarrow -196^\circ$. The -196° fraction contained methylsilane,¹³ while the -116° fraction was identified as acetone and some starting iodide.⁶³

6. The Reaction of Ammonium Thiocyanate with Chloromethylsilane

Summary: $\text{SiH}_3\text{CH}_2\text{Cl}$ was allowed to interact with excess NH_4CNS at room temperature. No reaction products were detected.

Experiment A: Ammonium thiocyanate (10 millimoles) was dried in a 250-ml. reaction flask by evacuating the flask for an hour. $\text{SiH}_3\text{CH}_2\text{Cl}$ (5 millimoles) and degassed acetone were condensed into the flask and allowed to warm to room temperature for ~ 16 hours. The volatile products were distilled: $\text{R.T.} \rightarrow -96^\circ \rightarrow -196^\circ$. The -196° fraction contained a small amount of acetone, while the -96° fraction was identified by infrared spectra as acetone plus a small amount of $\text{SiH}_3\text{CH}_2\text{Cl}$.⁶³

7. The Reaction of Silver Thiocyanate with Iodomethylsilane

Summary: $\text{SiH}_3\text{CH}_2\text{I}$ was allowed to react with excess AgCNS at 0° . No reaction products were detected.

Experiment A: Silver thiocyanate (9 millimoles) was dried in a reaction flask by evacuating the flask for an hour. $\text{SiH}_3\text{CH}_2\text{I}$ (5 millimoles) was condensed into the flask and allowed to warm to 0° for 2 days. An infrared spectrum of the volatile products showed that it consisted of acetone and some $\text{SiH}_3\text{CH}_2\text{I}$.⁶³

8. The Reaction of Potassium Thiocyanate and Chloromethylsilane

Summary: $\text{SiH}_3\text{CH}_2\text{Cl}$ and KCNS were allowed to interact in dimethylformamide at 0° . The only product detected was methylsilane.

Experiment A: Potassium thiocyanate (8 millimoles) was placed in a reaction flask and dried by simultaneously heating and evacuating the flask. Degassed dimethylformamide (~5 ml.) and $\text{SiH}_3\text{CH}_2\text{Cl}$ (4.9 millimoles) were condensed into the flask. The flask was then immersed in an ice bath for ~16 hours and the volatile products distilled: R.T. \longrightarrow -96° \longrightarrow -196° . The infrared spectrum of the -196° fraction identified it as methyl silane.¹³ There was no evidence for a silicon hydride with a thiocyanate group in the -96° fraction.

G. The High Resolution Proton Magnetic Resonance Spectra of 3-Germylpropene, 3-Silylpropene and 3-Monofluorosilylpropene

1. Preparation of Samples

The proton magnetic resonance (pmr) spectra of 3-germylpropene, 3-silylpropene and 3-monofluorosilylpropene were measured at a concentration of 20 v/v% in deuteriochloroform. In addition, a sample of 3-silylpropene was run at a concentration of 90 v/v%. The samples were degassed and sealed in 5 mm. nmr tubes in vacuo. Tetramethylsilane (TMS, ~1%) was added as an internal standard.

2. Spectra

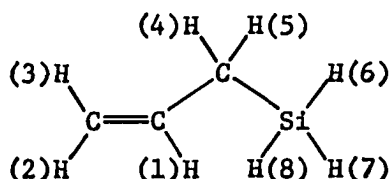
Pmr spectra of 3-germylpropene and 3-silylpropene were recorded on the R-20 60 MHz. spectrometer and were calibrated using the side band method and graphical interpolation. The pmr spectra of 3-monofluorosilylpropene were recorded on the 100 MHz. HA-100 spectrometer and were calibrated by using the monitor control switch to determine distance in

Hz. from the lock signal. The HA-100 was also used in conjunction with a V-4341 Variable Temperature accessory. A few spectra were recorded on the 250 MHz. spectrometer for comparison with spectra obtained on the other two instruments.

Several sweeps (a minimum of 6) of each portion of the spectrum were taken, 50% each in the direction of increasing and decreasing fields. The position of each peak was measured in cm. from a reference side band (when the R-20 was used) or calibration mark (when the HA-100 was used) on a Bruning Neoglide Drafting Machine and an average obtained in Hz. by means of the computer program CYCLIST.¹¹⁷ The printout lists line frequencies referenced to TMS as 0 Hz.

3. First-Order Analysis of Spectra

As an example of the first-order analysis of the spectra, the case of 3-silylpropene will be considered. The numbering scheme is indicated in Formula I.



Formula I

Referring to the pmr spectrum of 3-silylpropene (Figure II-X or II-Y), one observes two distinct groups of lines, the group at higher field consisting of three subgroups.

The lines at lowest field are due to proton 1 (see also Figure II-Z). A doublet arises from splitting by proton 3 ($J_{1,3} \approx 17$ Hz.),

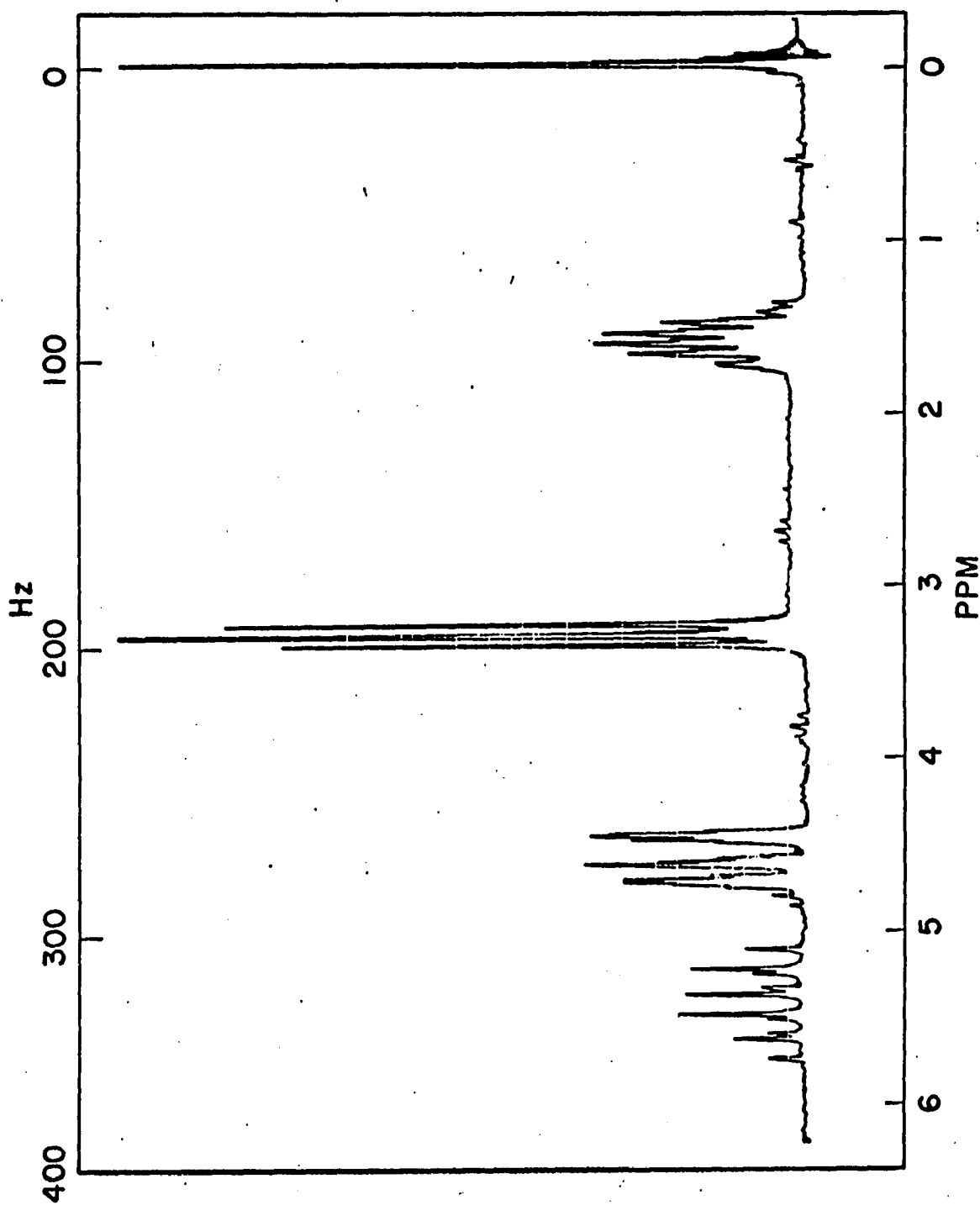


Figure II-W - Proton Magnetic Resonance Spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$ at 600 Hz. Sweep Width (60 MHz.)

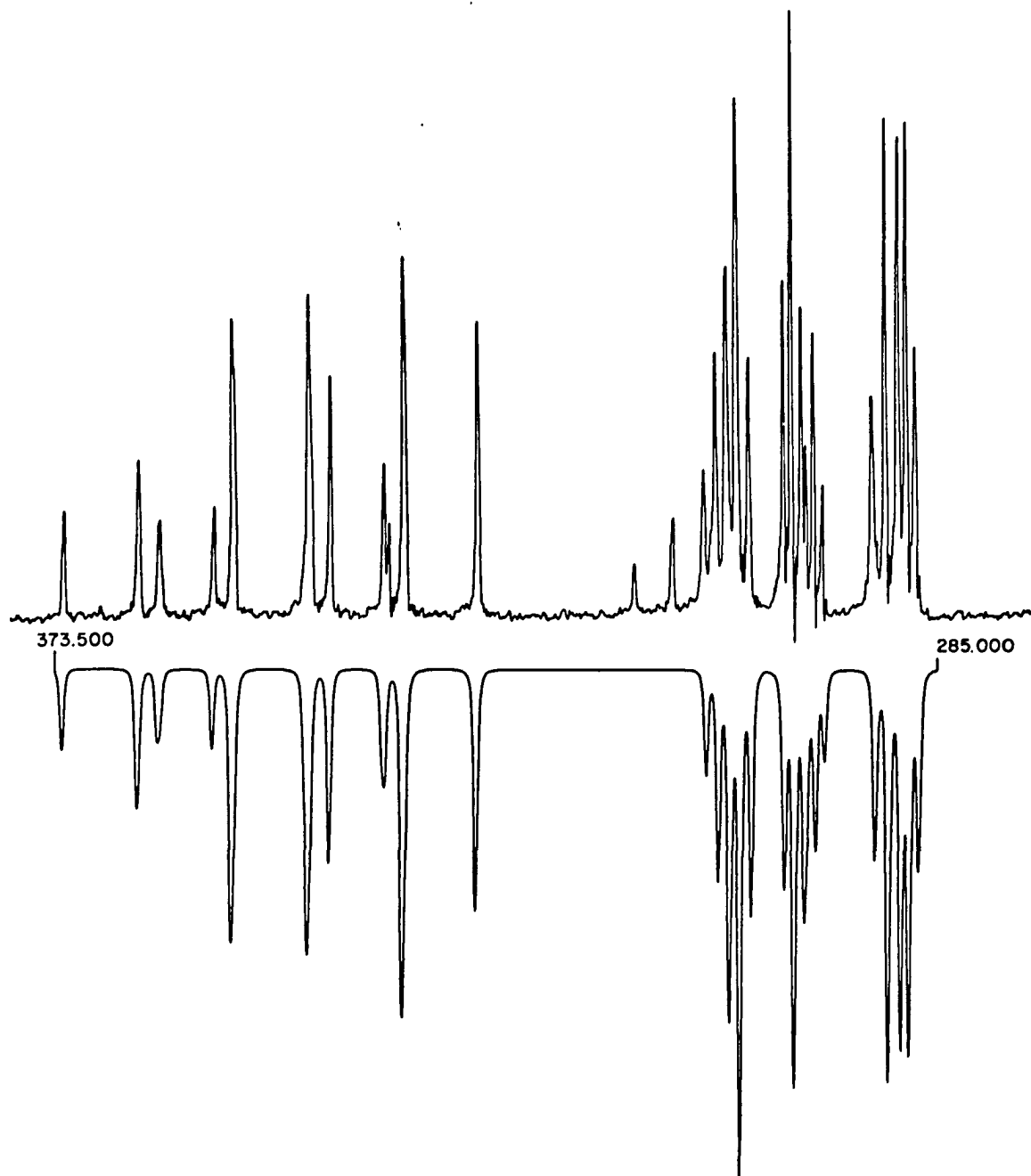


Figure II-X - Experimental and Calculated Proton Magnetic Resonance Spectra of $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$ (100 MHz.; $-\text{CH}_2-$ and $\text{CH}_2=$ Resonances)

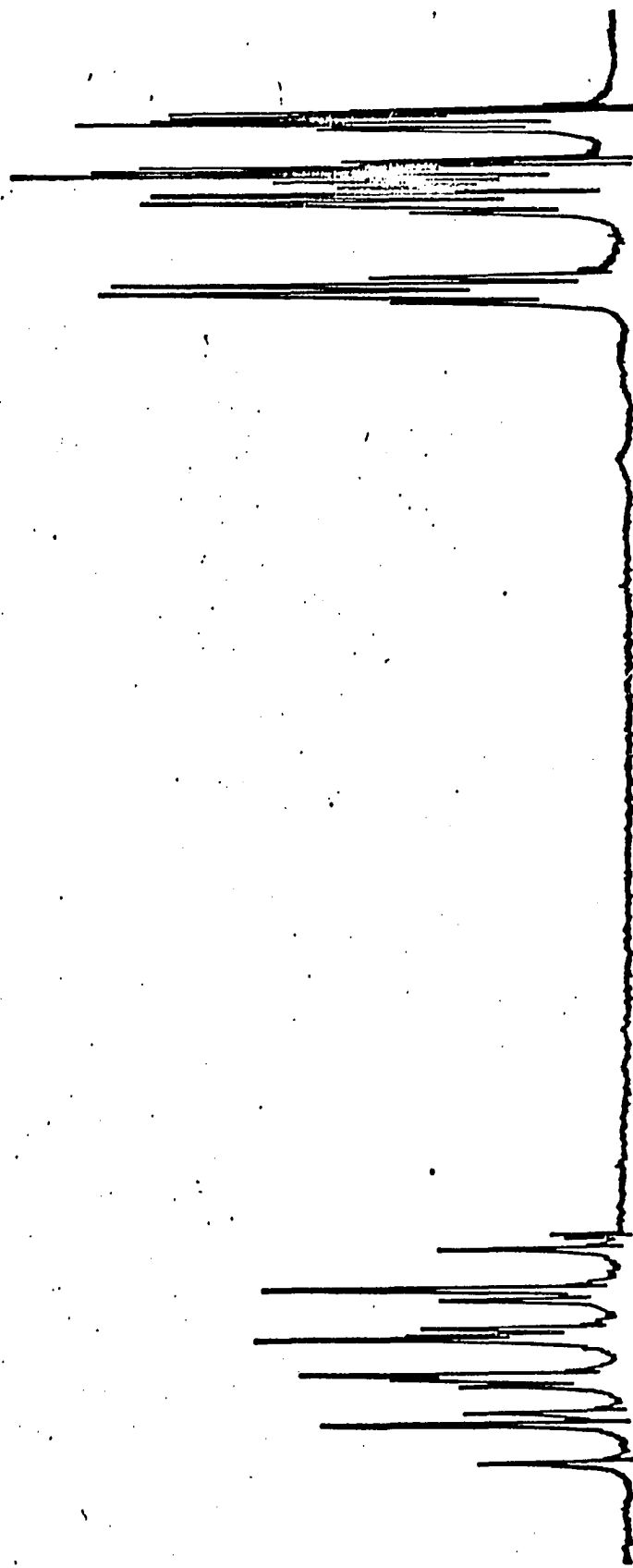


Figure II-Y - Proton Magnetic Resonance Spectrum of $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$ at 300 Hz. Sweep Width (250 MHz.; $-\text{CH}_2-$ and $\text{CH}_2=$ Resonances)

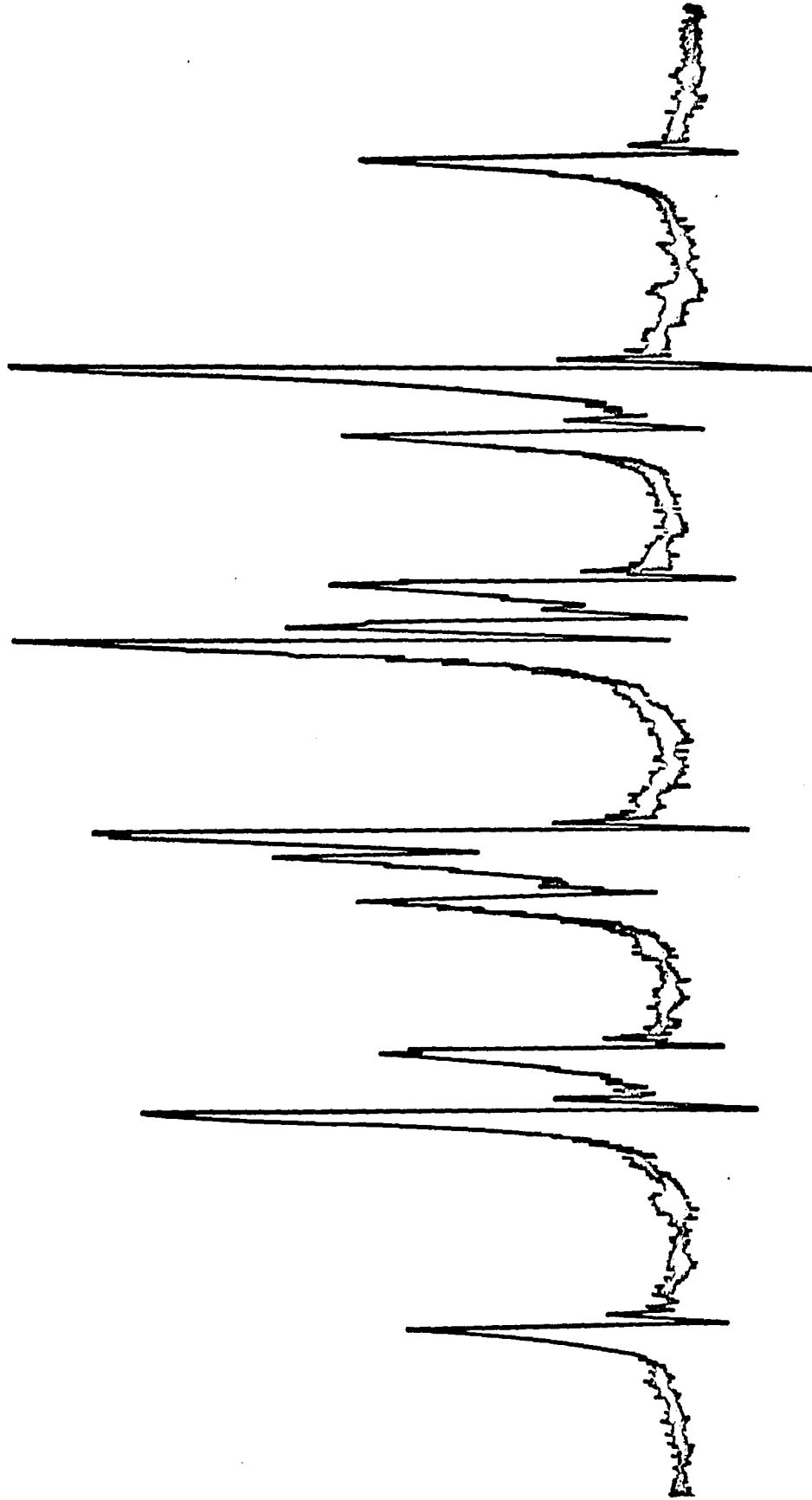


Figure II-Z - $-CH_2-$ Proton Resonance at 90 Hz. Sweep Width (250 MHz.; for $CH_2=CHCH_2SiH_3$)

which is further split into doublets by proton 2 ($J_{1,2} \approx 10$ Hz.) and finally into triplets by proton 4 ($J_{1,4} \approx 8$ Hz.).

The three subgroups at higher field in Figure II-X or II-Y were considered to originate from protons 2 and 3. The subgroup having the larger peak-to-peak distances was assigned to proton 3, for the trans coupling constant ($J_{1,3}$) is generally larger than the cis ($J_{1,2}$). The three subgroups are in actuality two doublets ($J_{1,2}$ and $J_{1,3}$), the subgroup at highest field being the result of an overlapping of the upper-field members of each doublet. (In Figure II-AA, a spectrum recorded on the 250 MHz. spectrometer does not show this overlap and the two doublets arising from $J_{1,2}$ and $J_{1,3}$ can be clearly distinguished.) These doublets are further split by the olefinic proton not in question (i.e., by proton 2 when proton 3 is under consideration) into doublets ($J_{2,3} \approx 2$ Hz.) and into triplets by the equivalent protons, 4 and 5 ($J_{2,4} \approx 1$ Hz., $J_{3,4} \approx 1.5$ Hz.).

Further upfield are two groups, which are shown in Figure II-W. First is a triplet, obviously due to the SiH_3 protons split by the equivalent protons, 4 and 5 ($J_{4,6} \approx 4$ Hz.). In the case of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ (Figure II-BB), it may be seen that a doublet of triplets results from the splitting of the SiH_2 protons first by fluorine, and then by protons 4 and 5.

Finally, at highest field, a complex group of lines (Figures II-W, II-DD and II-EE) is assigned to protons 4 and 5, and may be broken down into a doublet ($J_{1,4} \approx 8$ Hz.) of quartets ($J_{4,6} \approx 4$ Hz.) of doublets ($J_{3,4} \approx 1.5$ Hz.) of doublets ($J_{2,4} \approx 1$ Hz.), 32 lines in all. (In the fluorosilylpropene case, there is a further splitting by fluorine, giving a total of 64 lines.)

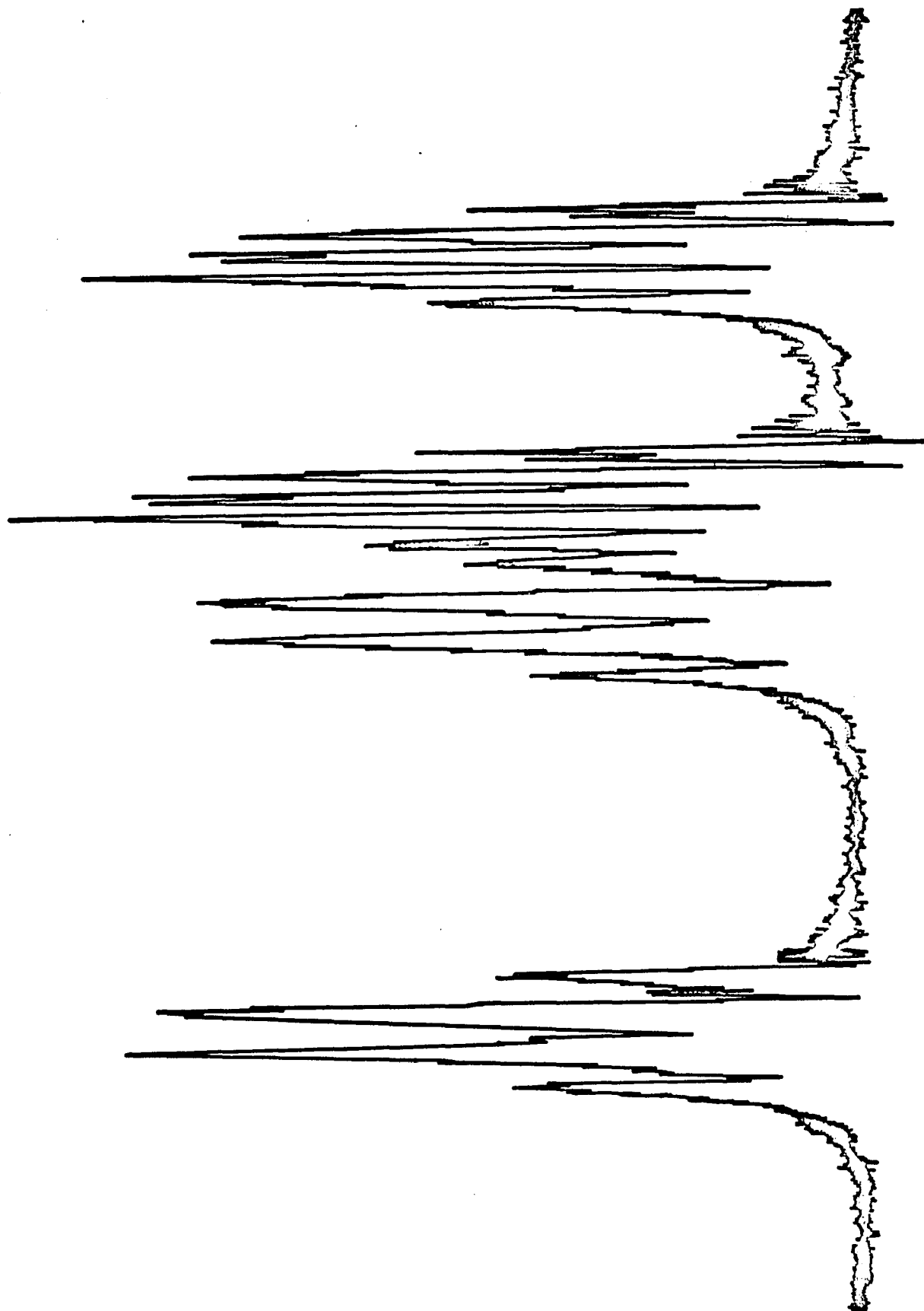


Figure II-AA - CH₂=CHCH₂SiH₃ Proton Resonance at 90 Hz. Sweep Width (250 MHz.); for CH₂=CHCH₂SiH₃

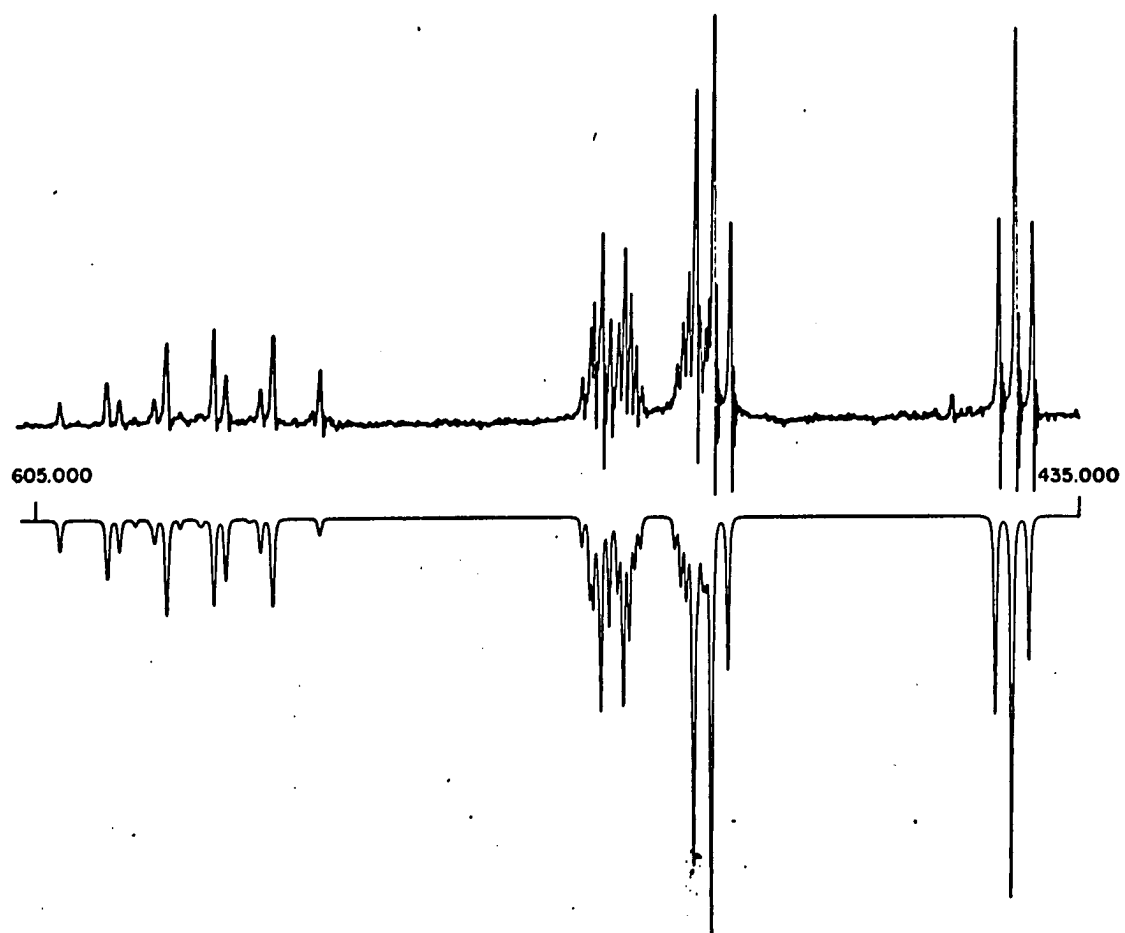


Figure II-BB - Experimental and Calculated Proton Magnetic Resonance Spectra of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ (100 MHz.; $-\text{CH}_2-$, $\text{CH}_2=$ and SiH_2 Resonances)

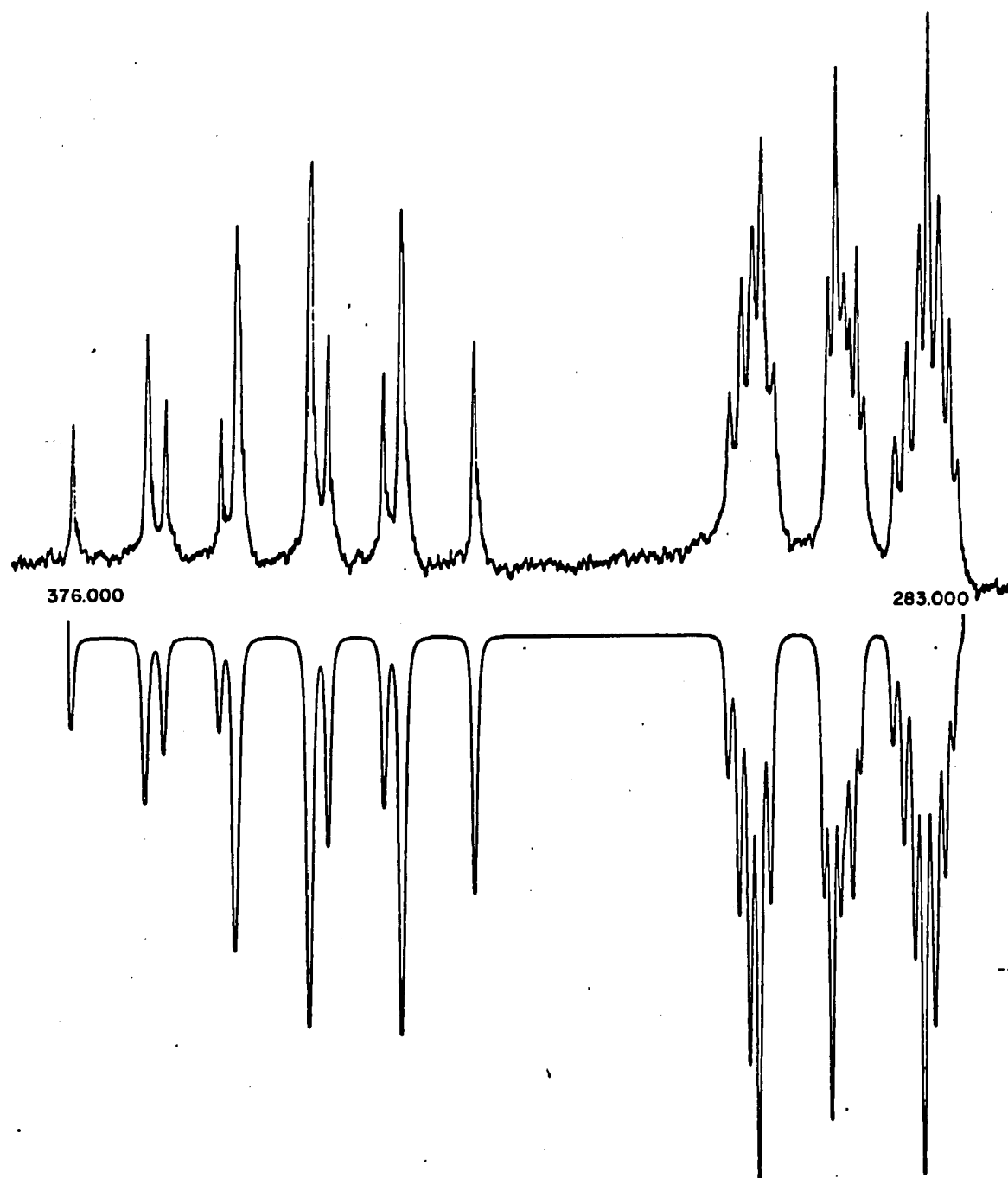


Figure II-CC - Experimental and Calculated Proton Magnetic Resonance Spectra of $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$ (100 MHz.; $-\text{CH}_2-$ and $\text{CH}_2=$ Resonances)

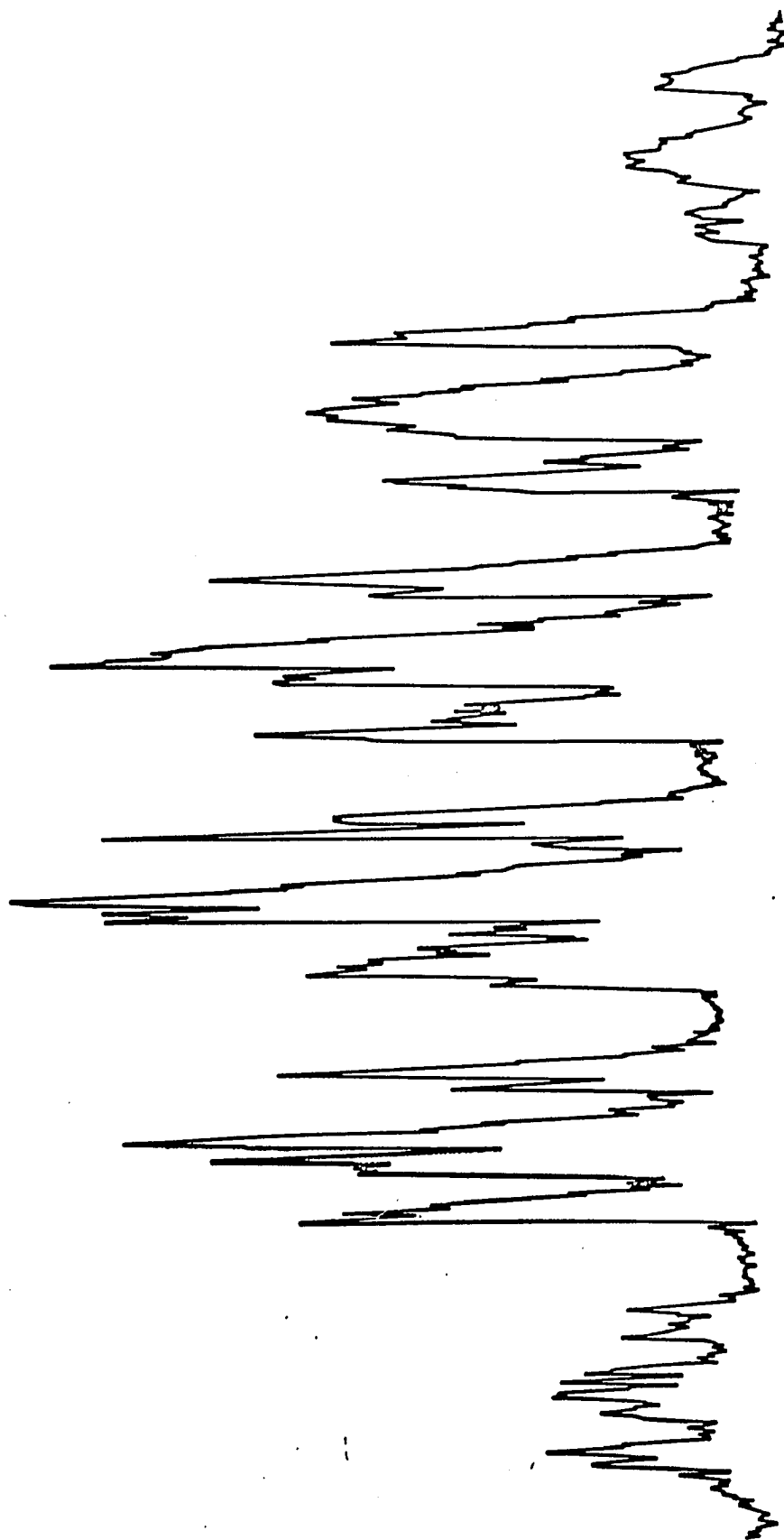


Figure II-DD - =CH- Proton Resonance at 30 Hz. Sweep Width
(60 MHz.; for $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$)

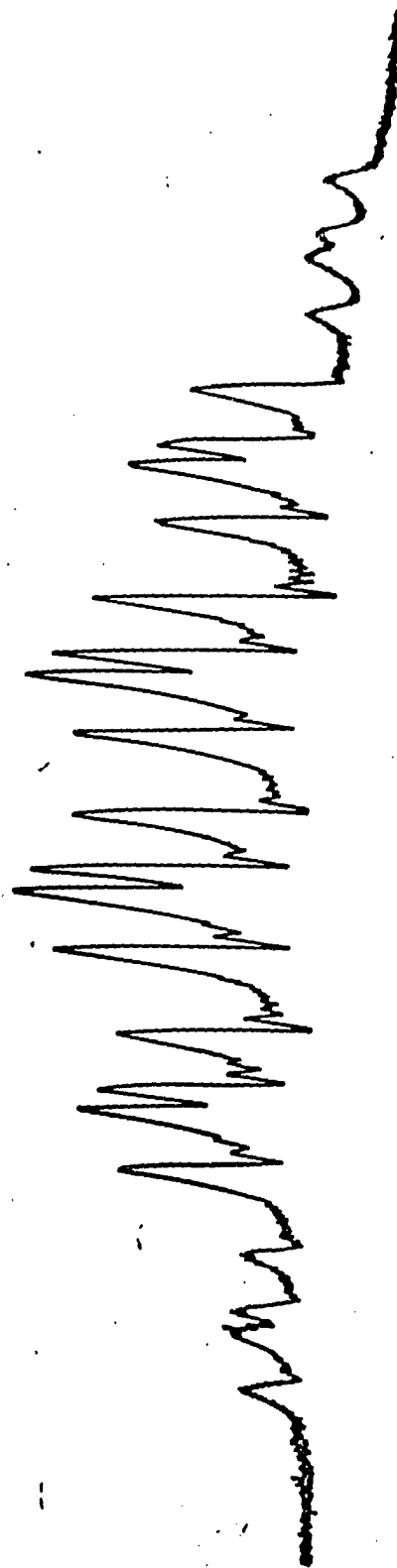


Figure II-EE - =CH- Proton Resonance at 30 Hz. Sweep Width
(250 MHz.; for CH₂=CHCH₂SiH₃)

4. LAOCN 3 Analysis of Spectra

The first order estimated values for the chemical shifts and coupling constants of each compound were inputted to the iterative least-squares computer program LAOCN 3.⁴⁰ Negative coupling constants were introduced considering previous analyses.^{23-26,206} A theoretical spectrum was calculated and the theoretical line positions and intensities were compared with experimental spectra. Corrections of the original parameters were made where necessary and were resubmitted together with the previously measured line frequencies. An iterative calculation is performed, bringing the calculated lines as close as possible to the experimental lines. The "best values" for the chemical shifts and coupling constants are thus obtained as well as the newly calculated line frequencies and intensities plus the error between the new theoretical spectrum and the experimental spectrum. Parameters and line assignments were further corrected if necessary and resubmitted. The procedure was repeated until reasonable agreement was reached between calculated and observed spectra. An indication of this agreement is the reduction of the RMS error to approximately 0.05. With the aid of the program SPLOT, a calculated spectrum was plotted on a Cal-Comp plotter and compared with the experimental (Figures II-X, II-BB and II-CC).

The LAOCN 3 program accepts only up to 7 spins. In $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$ and $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$, however, there are 8 protons. In order to perform the calculations, the GeH_3 and SiH_3 protons were ignored completely, essentially eliminating $J_{4,6}$ and leaving only 5 spins. By ignoring these protons, the LAOCN 3 predicted spectrum contains only 8 lines in the region of protons 4 and 5 (Figure II-GG) instead of the

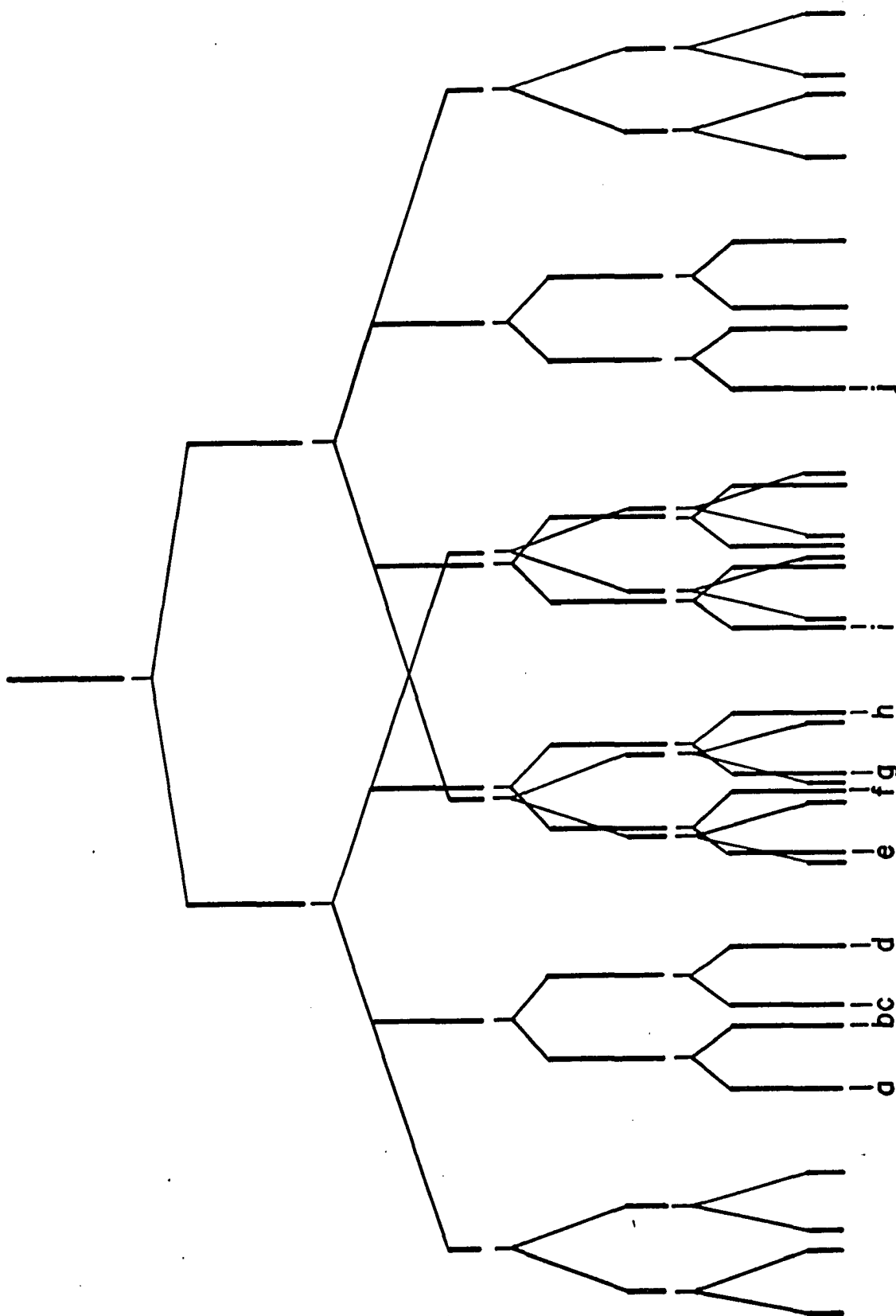


Figure II-FF - Calculated Proton Magnetic Resonance of $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$ (=CH- Resonance)

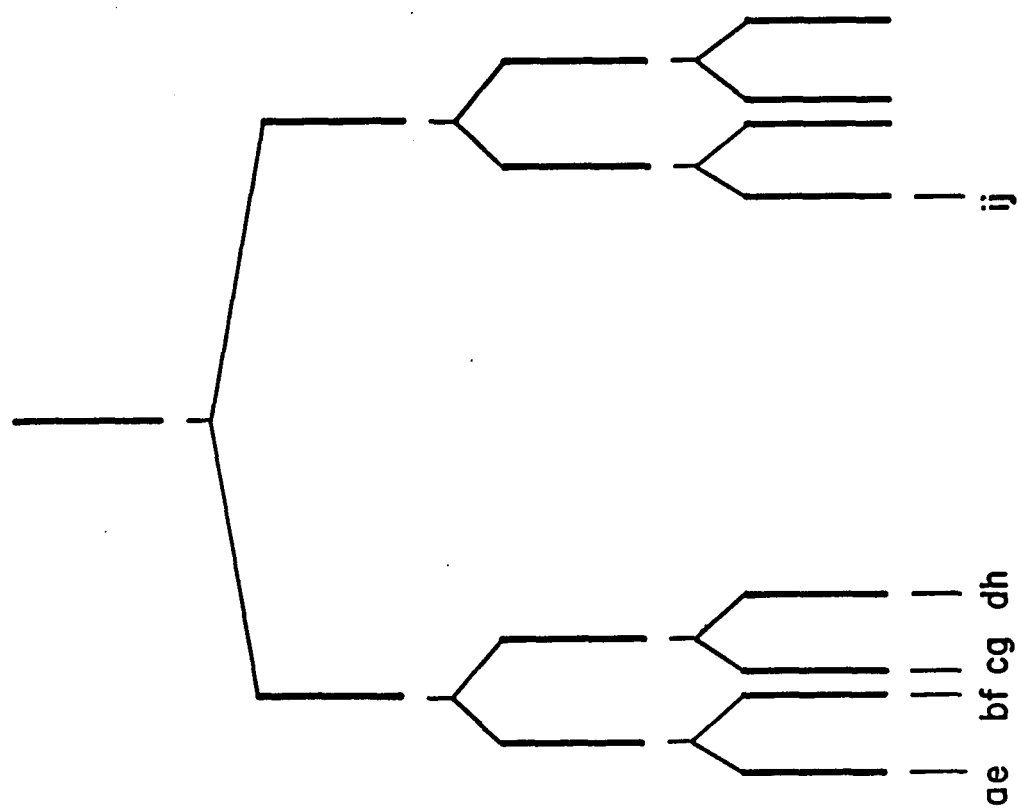


Figure II-GG - Calculated Proton Magnetic Resonance of $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$ (=CH - Resonance)
Ignoring SiH_3 Splitting

experimentally obtained 32 lines (Figure II-DD or II-EE). The chemical shift and coupling constants for the equivalent 4 and 5 protons is obtainable by averaging certain lines in the observed spectrum and assigning the resulting values to lines in the predicted spectrum.

An example may serve to clarify the procedure. Referring to Figure II-FF, it will be noticed that the various splittings produce six main groups of lines. Focusing on the second and third groupings from the left, it is possible to average the 8 more-intense lines into 4; line a is averaged with line e to give a line corresponding to line ae in Figure II-GG. By the same method, lines bf, cg and dh in Figure II-GG are obtained. The procedure is repeated for the fourth and fifth groupings from the left in Figure II-FF, e.g., line i and line j are averaged to give line ij in Figure II-GG. The 8 lines thus obtained are assigned and inputted to the LAOCN 3 program; all the coupling constants are represented except $J_{4,6}$ and the chemical shift is located by averaging, for example, lines dh and ij.

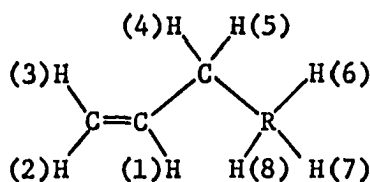
An additional calculation was performed on 3-silylpropene considering the two subspectra $a_{+\frac{1}{2}}, a_{-\frac{1}{2}}$ (I) and $a_{+\frac{3}{2}}, a_{-\frac{3}{2}}$ (II), where $a_{\pm n}$ corresponds to the quantum states of the z component of the total angular momentum of the silyl protons.²⁰⁸ I was calculated first, using the parameters previously obtained in the 5-spin case, but with the silyl protons considered as a single spin. Additional information for the resulting 6-spin system was submitted as needed. The results were similar to the parameters obtained considering a 5-spin system. In order to calculate II, it was necessary to multiply the coupling constants of the silyl protons by 3, since I and II have statistical weights of 3 and 1 respectively. The intensities of the resulting calculation would

therefore have to be reduced by 1/3 of their calculated value. When this was done, however, it was found that the resolution of the experimental spectra was not adequate to permit assignment of lines and the calculation of II was abandoned. The results of I seemed sufficient to indicate the correctness of using either a 5- or a 6-spin system.

In the analysis of 3-fluorosilylpropene, two subspectra were also considered: an upper-field and a lower-field spectrum arising from splitting by fluorine. After the two subspectra were calculated to the minimum RMS error, the line positions plus intensities were combined and plotted together via SPLOT and the Cal-Comp plotter (Figure II-BB). The difference between the two subspectra is a measure of the coupling between fluorine and the various protons in the molecule. The results of the three LAOCN 3 analyses are contained in Tables II-41, II-42 and II-43.

Table II-41

Proton Magnetic Resonance Data for $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$
and $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$



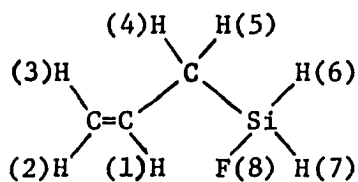
	R=Si 20% in CDCl_3			R=Si 90% in CDCl_3		R=Ge 20% in CDCl_3	
	<u>Chemical Shifts</u>						
	<u>Hz.</u> ^a	<u>Hz.</u> ^b	<u>τ</u>	<u>Hz.</u> ^b	<u>τ</u>	<u>Hz.</u> ^a	<u>τ</u>
w(1)	350.07	350.08	4.166	346.58	4.225	352.75	4.121
w(2)	294.26	294.20	5.097	291.88	5.135	291.20	5.147
w(3)	298.71	298.56	5.023	296.36	5.061	297.71	5.038
w(4)=w(5)	102.30	102.33	8.294	98.80	8.353	113.92	8.101
w(6)=w(7)	213.01 ^c	212.88	6.451	213.19	6.447	215.79 ^c	6.404
	<u>Coupling Constants (Hz.)</u>						
$J_{1,2}$	10.03	10.06		10.07		10.08	
$J_{1,3}$	16.96	16.91		16.92		17.01	
$J_{1,4}$	7.72	7.73		7.75		7.97	
$J_{1,6}$	--	-0.01		-0.01		--	
$J_{2,3}$	1.76	1.69		1.75		1.82	
$J_{2,4}$	-1.05	-1.05		-1.05		-0.93	
$J_{2,6}$	--	0.18		-0.001		--	
$J_{3,4}$	-1.38	-1.39		-1.46		-1.33	
$J_{3,6}$	--	0.09		0.003		--	
$J_{4,6}$	3.89 ^c	3.84		3.91		3.55 ^c	

^a Calculated as a 5-spin system.

^b Calculated as a 6-spin system.

^c Measured directly from experimental spectra.

Table II-42

Proton Magnetic Resonance Data for $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ 

	Higher-Field Subspectrum	Lower-Field Subspectrum	Average	
<u>Chemical Shifts</u>				
	<u>Hz.</u>	<u>Hz.</u>		
w(1)	578.398	578.653	578.526	4.215
w(2)	504.220	504.400	504.310	4.957
w(3)	506.293	506.400	506.288	4.937
w(4)=w(5)	187.824	193.463	190.644	8.094
w(6)=w(7)	445.895	495.000	470.448	5.296
<u>Coupling Constants (Hz.)</u>				
J _{1,2}	10.160	10.138	10.149	
J _{1,3}	17.042	17.039	17.040	
J _{1,4} =J _{1,5}	7.826	7.804	7.815	
J _{1,6} =J _{1,7}	0.003	-0.007	-0.005	
J _{2,3}	1.655	1.654	1.654	
J _{2,4} =J _{2,5}	-1.002	-0.998	-1.000	
J _{2,6} =J _{2,7}	0.001	0.000	0.000	
J _{3,4} =J _{3,5}	-1.455	1.451	-1.453	
J _{3,6} =J _{3,7}	0.000	-0.000	0.000	
J _{4,6} =J _{4,7}	2.751	2.746	2.748	
J _{5,6} =J _{5,7}	2.751	2.746	2.748	

Table II-43

Fluorine-Hydrogen Coupling Constants for $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}^{\text{a,b}}$

	$J_{1,\text{F}}$	$J_{2,\text{F}}$	$J_{3,\text{F}}$	$J_{4,\text{F}}=J_{5,\text{F}}$	$J_{6,\text{F}}=J_{7,\text{F}}$
Hz.	0.255	0.180	0.011	5.639	49.105

^a Obtained by subtracting the higher-field subspectrum chemical shift from the lower-field subspectrum (Table II-42).

^b For numbering system, see formula in Table II-42.

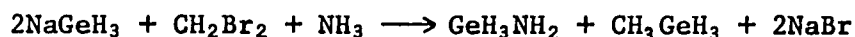
DISCUSSIONA. The Use of Alkali Metal Derivatives of Germane in the Synthesis of Organogermanes1. Previous Investigations

Alkali metal derivatives of germane have been successfully used as intermediates in the preparation of a wide variety of organogermanium hydrides. Several examples of this use and some of the methods employed have been mentioned in the introduction. In the present research, the reactions studied concerned only two of these methods: (1) the reaction of organohalides with NaGeH_3 (solid) prepared from the interaction of germane and sodium-liquid ammonia solutions, and (2) the reaction of organohalides with a solution of KGeH_3 prepared from the reaction of germane with potassium in hexamethylphosphortri-*amide* (HMPT).

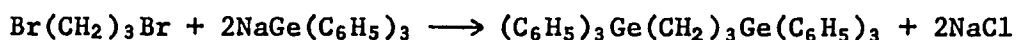
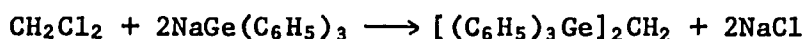
Solid sodium germal was prepared in order to eliminate all extraneous solvent effects. At room temperature, the white sodium germal turns brown, but reactions with this latter material still proceed to some extent.

HMPT was used as a solvent for the preparation of KGeH_3 from germane and potassium in order to reduce some of the side reactions mentioned in the introduction, e.g., a solvolysis type reaction with ammonia. Caution must be observed, though, to maintain the solution of potassium in HMPT below 10° . Failure to do so may result in alkali metal attack on the solvent, producing volatile materials thought to contain dimethylamine. If the blue alkali metal solution changes to a brown color, the mixture must be discarded and the preparation procedure repeated from the beginning.

Previous attempts to prepare $\text{GeH}_3(\text{CH}_2)_n\text{GeH}_3$, where $n = 1, 2, 3$, have met with mixed success. Teal and Kraus reacted sodium germyl with dichloromethane in liquid ammonia and produced methylgermane and amino-germane according to the proposed reaction ¹⁸⁸

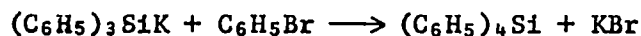


Sodium triphenylgermyl does react with dihalides to yield the corresponding bistrisphenylgermyl derivatives according to the following reactions:^{120,177}

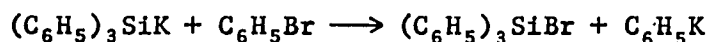


However, a reaction of $\text{NaGe}(\text{C}_6\text{H}_5)_3$ with $(\text{CH}_2)_2\text{Br}_2$ yielded 87% hexaphenyl-digermane and presumably the unsaturated hydrocarbon. In the above reaction with methylene chloride, side reactions occurred involving the solvent (liquid ammonia) to yield $(\text{C}_6\text{H}_5)_3\text{GeNH}_2$ and $(\text{C}_6\text{H}_5)_3\text{GeCH}_3$.

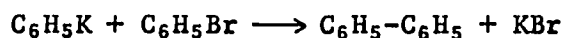
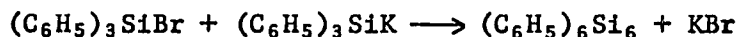
Brook and Wolfe found that the reaction between potassium triphenyl and phenylbromide not only yielded the desired coupling product,³¹



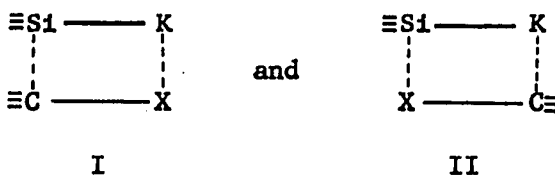
but that it also proceeded by "halogen-metal interconversion", i.e.



Other observed products were explained by the following reactions:

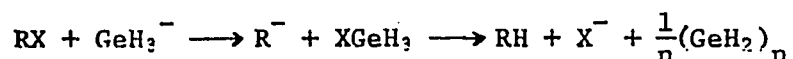


It was proposed that there exist two competitive four-centered transition states which lead to the observed products:

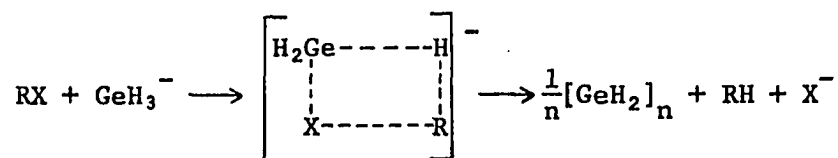


If X is too weakly electronegative, the suggestion was that state I is not favored.

Dreyfus and Jolly have added to this proposal when, during the course of this research, they reported the preparation of $(\text{GeH}_3)_2\text{CH}_2$ from the reaction of CH_2Cl_2 or CH_2Br_2 with KGeH_3 in bis(methoxyethyl) ether (diglyme).⁵³ Methylgermane was among the products of the reaction. To explain the presence of CH_3GeH_3 , the assertion was made that the reaction of an alkali metal derivative of germane with an organic halide may proceed in two different ways. One is a nucleophilic attack of the germyl anion on carbon and the other is a nucleophilic attack of the germyl anion on the halogen. A possible mechanism for the reaction of potassium germyl with an alkyl halide to give the reduced alkane assumes the latter attack:



When $\text{R} = \text{C}_6\text{H}_5$, $\text{X} = \text{Br}$ and the germyl hydrogens were replaced by deuterium, it was discovered that deuterium replaced the bromine to form deutorobenzene. Thus the hydrogen on RH does indeed originally come from the germyl anion. It follows that a phenyl anion (R^- in the above equation) must deprotonate the bromogermane in preference to the solvent. However, $\text{C}_6\text{H}_5\text{Na}$ and excess GeH_3Br in diglyme resulted mainly in solvent cleavage. If a free phenyl anion (R^-) were present in the reaction of $\text{C}_6\text{H}_5\text{Br}$ and GeH_3^- , one would also expect diglyme cleavage, not the production of C_6H_6 . An alternate mechanism is therefore proposed to explain the formation of RH -- a four-centered transition state:

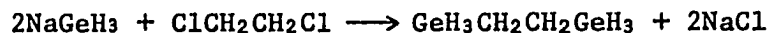


The products of the reactions in the present research are most likely results of the competing reaction mechanism mentioned above.

2. The Investigated Reactions

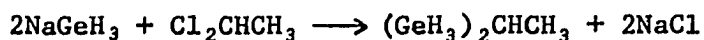
a. Digermylalkanes

The preparation of 1,2-digermylethane was accomplished by the interaction of solid NaGeH_3 with 1,2-dichloroethane at room temperature for ~20 hours:



The products could be reasonably purified in the vacuum line, though final purification of $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ from the starting dichloride could only be accomplished by gas chromatography using a heated column. The yield of $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ was 45% and the product appeared to be thermally stable at room temperature.

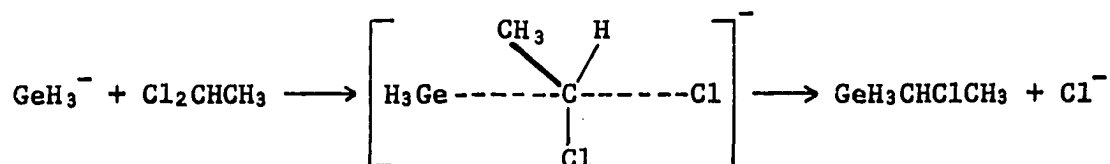
1,1-Digermylethane was prepared by allowing 1,1-dichloroethane to react with solid sodium germyl at 0° for 24 hours:



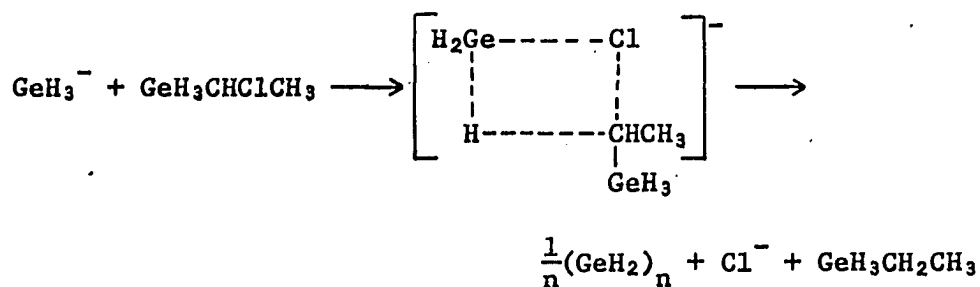
Only a small amount of material (~0.5% yield) resulted after purification of the reaction products by gas chromatography. Identification of $(\text{GeH}_3)_2\text{CHCH}_3$ was based on mass and proton magnetic resonance spectra.

In the reaction of sodium germyl with both 1,1- and 1,2-digermylethane, monogermylethane was produced, though only a small amount in the 1,2-digermylethane case. An explanation for the major occurrence of $\text{GeH}_3\text{C}_2\text{H}_5$ from the 1,1-digermylethane reaction may be the steric unfavorability for a second germyl group to substitute onto carbon.

Since some of the product does form, a second explanation may be needed. Nucleophilic attack by the germyl anion on carbon would be facilitated by the electronegative nonleaving chlorine.



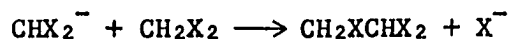
Once substituted for chlorine, the germyl group, being less electronegative than chlorine, would not as readily facilitate nucleophilic attack on carbon by a second germyl anion and nucleophilic attack on the second chlorine may now become preferential.



In the case of 1,2-dichloroethane, steric hindrance does not prevent the substitution of germyl for chlorine on either end of the molecule. The long reaction time required for a sufficient yield of 1,2-digermylethane indicates that the nucleophilic attack on carbon is slow. This may be due to the absence of an electronegative group which would favor this kind of attack.

It was suggested by Dreyfus and Jolly that digermylethane could result from deprotonation of the halomethanes by potassium germyl.⁵³

The resulting carbanions may then attack another halomethane to yield a haloethane. Further attack by a germyl anion produces the digermylethane. The reaction sequence is given below:



These authors report seeing three small peaks under the septet arising from $(\text{GeH}_3)_2\text{CH}_2$ (9.67 τ) and suggest they may be part of a quartet arising from digermylethane. As has been shown in this research, however, the peaks at highest field in $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ occur at 8.84 τ . It is therefore doubtful that Dreyfus and Jolly had any 1,2-digermylethane present in their reaction products.

b. Allyl Germane

Allyl bromide reacted with solid sodium germyl to give a 15% yield of $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$. All the products detected are consistent with nucleophilic attack by the germyl anion on carbon. Previously, the compound had been prepared by the reduction of the trichlorogermyl compound with lithium hydride in 28% yield:¹⁴⁵



The disadvantage of using the latter reduction method for preparing allyl germane is that the intermediate trichloro derivative is not readily available. The present method involving the easily prepared intermediate NaGeH_3 thus appears to be a much better synthesis.

c. Germylmethyl Methyl Sulfide

The preparation of germylmethyl methyl sulfide was attempted by the reaction of chloromethyl methyl sulfide with both KGeH_3 in HMPT

and solid NaGeH_3 . The desired product was detected only in the former case. The reason for this apparent specificity is ambiguous, for the analogous ether, $\text{GeH}_3\text{CH}_2\text{OCH}_3$, was prepared by the reaction of $\text{ClCH}_2\text{OCH}_3$ with solid NaGeH_3 .⁷⁷ There may have been some minor differences in reaction conditions between the two reactions which would account for the observed results, but they are not obvious. In any case, a fair amount of material was prepared which was shown to be $\text{GeH}_3\text{CH}_2\text{SCH}_3$ from precise mass measurement and proton magnetic resonance data.

Observations while attempting to determine the melting point and vapor pressure of the compound led to the conclusion that the thermal stability in the liquid phase was very low and that a polymer formed which possessed a very low vapor pressure at room temperature. This polymer therefore did not add measurably to the infrared spectrum, and the material in the infrared cell was presumed to contain only $\text{GeH}_3\text{CH}_2\text{SCH}_3$. The latter compound appears to be more stable in the gaseous state than the liquid state.

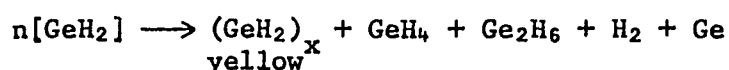
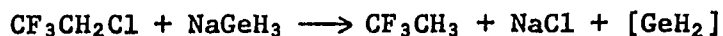
d. Vinyl Germane

Vinyl germane has been prepared by previous workers in 58% yield by the reduction of vinyltrichlorogermane with lithium aluminum hydride in diglyme at 115° .²⁸ An attempt was made to synthesize the compound by the reaction of vinyl bromide with solid sodium germyl in order to eliminate the tedious preparation of the intermediate trichloride. A small amount of vinyl germane was prepared by the new method, but the yield was much smaller than previously reported²⁸ and the investigated preparation does not threaten to replace the previous method.

e. The Interaction of NaGeH_3 and $\text{CF}_3\text{CH}_2\text{Cl}$

The reaction of $\text{CF}_3\text{CH}_2\text{Cl}$ with solid sodium germyl may be

written as proceeding by nucleophilic attack on chlorine as evidenced by the detection of CF_3CH_3 and Ge_2H_6 in the reaction products. No $\text{CF}_3\text{CH}_2\text{GeH}_3$ was observed:



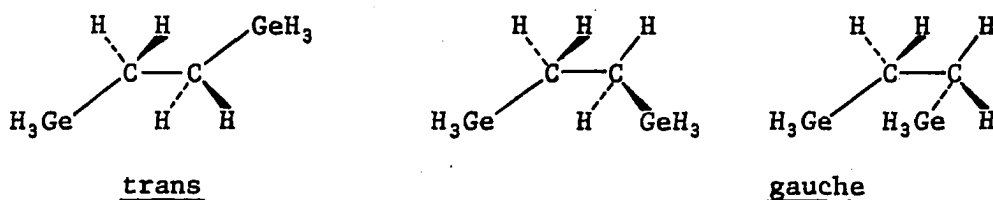
f. The Interaction of NaGeH_3 with ClCH=CHCl and ClCH_2CN

Both ClCH=CHCl and ClCH_2CN were recovered unchanged after interaction with solid sodium germyl. Evidently their C-Cl bonds are strong enough to resist attack by GeH_3^- under the conditions used.

3. Infrared, Proton Magnetic Resonance and Mass Spectra of Germyl Substituted Organic Compounds

a. Infrared Spectra

The infrared spectra of $\text{ClCH}_2\text{CH}_2\text{Cl}$ and $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ would be expected to share several features. The infrared spectrum of 1,2-dichloroethane has been thoroughly elucidated.¹³⁹ Raman and infrared spectra, dipole moment, electron diffraction, X-ray diffraction, nmr and some thermal properties have yielded data which demonstrate that this molecule exists in the trans (C_{2h}) and gauche (C_2) forms in the gaseous and liquid states, but only in the trans form in the solid state.¹³⁹ Raman and infrared spectra in the liquid and solid states have permitted the assignment of the appropriate frequencies to each form. Similar work was done in assigning frequencies to the gauche and trans forms of n-propylchlorogermanes.¹⁹⁰ It follows that 1,2-digermylethane may also exist in the gauche and trans form as well.



A comparison of the frequencies obtained in the infrared spectrum of $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ in the gas phase with the gauche and trans frequencies of $\text{ClCH}_2\text{CH}_2\text{Cl}$ seem to indicate that frequencies assignable to both trans and gauche forms are present under these conditions (Table II-7).

Table III-1 presents frequencies which are assignable to one or the other form and which were taken as indicating the presence of both forms of digermylethane.

Table III-1

Certain Frequencies Used in Assigning Trans and Gauche Forms
of 1,2-Digermylethane^a

Mode ^b	ClCH ₂ CH ₂ Cl ^c		Cl ₃ GeCH ₂ CH ₂ GeCl ₃ ^d		GeH ₃ CH ₂ CH ₂ GeH ₃
	trans	gauche	trans	gauche	
w(CH ₂)	1230	1264	--	--	1233,1290
ρ(CH ₂)	768	881	801	814	785,853
ρ(CH ₂)	--	--	698	743	700,728
ν(GeC)	--	--	664	590	622,605

^a Values reported in cm⁻¹. ^c Reference 139.

^b For explanation of symbols, see Appendix. ^d Reference 190.

The infrared spectral frequencies of certain absorptions of 1,2-digermylethane, germylemethyl methyl sulfide, methyl germane and ethyl germane are very similar to one another (Table III-2).

Table III-2

Comparison of Selected Absorption Frequencies of Various Organogermanes^a

	$\nu(\text{GeH}_3)$	$\nu_s(\text{CH}_2)$	$\delta_1(\text{GeH}_3)$	$\delta_2(\text{GeH}_3)$	$\nu(\text{Ge-C})$
$\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$	2074	2912	890 883	830	608 603
$\text{GeH}_3\text{CH}_2\text{SCH}_3$	2094 2083	2932 2924	883	840 834	650
$\text{GeH}_3\text{CH}_3^b$	2084	--	900	842	602
$\text{GeH}_3\text{CH}_2\text{CH}_3^c$	2085 2079 2072	2936 2925	884	835	624 613

^a Values reported in cm^{-1} .

^b Reference 91.

^c Reference 131.

The most notable difference is in the high Ge-C stretching frequency observed for $\text{GeH}_3\text{CH}_2\text{SCH}_3$ compared to frequencies found in other compounds. The electronegative group sulfur is most likely the cause of this shift.

Certain other infrared frequencies for these compounds can be readily assigned based on the assignments given for the spectra of related derivatives. Thus absorptions in the 2074-2094 region are undoubtedly due to the Ge-H stretching modes, those in the 2912-2932 region are the CH_2 symmetric stretching modes and those in the 834-900 region belong to one of the GeH_3 deformation modes. All these data are summarized in Table III-2.

b. Proton Magnetic Resonance Spectra

The proton magnetic resonance data for the two new germylethanes and three related compounds are presented in Table III-3.

Table III-3

Proton Magnetic Resonance Data for Selected Alkylgermanes

Compound	τ_{GeH_3}	τ_{CH_2}	τ_{CH_3}	$J_{\text{GeH}_3-\text{CH}_2}$	$J_{\text{GeH}_3-\text{CH}_3}$	$J_{\text{CH}-\text{CH}_3}$
$\text{GeH}_3\text{CH}_3^{\text{a}}$	6.55	--	9.71	--	4.22	--
$\text{GeH}_3\text{CH}_2\text{CH}_3^{\text{b}}$	6.45	9.21	8.95	--	--	--
$\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$	6.43	8.84	--	1.8	--	--
$(\text{GeH}_3)_2\text{CHCH}_3^{\text{c}}$	6.29	--	8.62	3.3	0.5	8.0
$(\text{GeH}_3)_2\text{CH}_2^{\text{d}}$	6.16	9.67	--	4.0	--	--

^a Reference 60.

^b Reference 130.

^c Values obtained from the initial sample on page 59.

^d Reference 53.

It can be seen that the data are all in the region expected and nothing particularly unusual is evident. The data were used mainly to characterize the compounds.

The proton magnetic resonance data for germylethyl methyl sulfide and some related compounds are presented in Table III-4.

Table III-4
Proton Magnetic Resonance Data for Germylmethyl Methyl Sulfide
and Some Related Compounds

Compound	$\tau_{\text{MH}_3}^{\text{a}}$	τ_{CH_2}	τ_{SCH_3}	$J_{\text{GeH}_3-\text{CH}_2}$
$(\text{CH}_3)_2\text{S}^{\text{b}}$	--	--	7.98	--
$\text{SiH}_3\text{SCH}_3^{\text{b}}$	5.71	--	7.98	--
$\text{GeH}_3\text{SCH}_3^{\text{b,c}}$	5.52	--	7.95	--
$\text{CH}_3\text{CH}_2\text{SCH}_3^{\text{d,e}}$	8.73	7.47	7.90	7
$\text{GeH}_3\text{CH}_2\text{SCH}_3^{\text{d}}$	6.26	7.87	7.82	3.37
$\text{GeH}_3\text{CH}_2\text{OCH}_3^{\text{c,f}}$	6.39	6.54	6.89	3.10

<p>^a M = C, Si, Ge (CH₃ attached to CH₂).</p> <p>^b Reference 202.</p> <p>^c In cyclohexane.</p>	<p>^d In CDCl₃.</p> <p>^e Reference 27.</p> <p>^f Reference 77.</p>
---	--

Wang and Van Dyke noticed that the chemical shifts of the methyl protons in the MH_3SCH_3 (M = C, Si and Ge) series of compounds remain essentially unchanged.²⁰²

It was further generalized that the chemical shift of the CH_3 protons on the CH_3SR derivatives were almost totally unaffected by the nature of R. It was thus interesting to note that a methylene group placed between sulfur and germanium caused the methyl chemical shift to move noticeably downfield. This is also the case in methylethyl sulfide, but the change between the latter compound's methyl chemical shift is not as great as the chemical shift in the corresponding germyl compound.

The methylene group of $\text{GeH}_3\text{CH}_2\text{SCH}_3$ is at higher field than the corresponding ether, as anticipated from the greater electronegativity

of oxygen compared to sulfur. One would expect the same effect to be seen in the chemical shift of the germyl group. However, the opposite is observed. This general trend of the shifts of the α and β protons has been noted by other workers in a variety of other systems, e.g., $\text{CH}_3\text{CH}_2\text{X}$ and $\text{SiH}_3\text{SiH}_2\text{X}$, and is not that surprising.¹⁹⁸

c. Mass Spectra

The mass spectra of various digermyl derivatives are given in Table III-5.

Table III-5

Mass Spectral Data for Some Digermyl Organic Derivatives

Heavy Atom Skeleton	Relative Intensity (%)		
	$\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$	$(\text{GeH}_3)_2\text{CHCH}_3$	$(\text{GeH}_3)_2\text{CH}_2^a$
Ge_2C_2^+	25.9	34.3	--
Ge_2C^+	--	2.1	100.0
Ge_2^+	82.1	100.0	14.8
GeC_2^+	100.0	68.0	--
GeC^+	--	--	24.7
Ge^+	65.3	47.8	7.3

^a Reference 53.

It is interesting to note the presence of the ion Ge_2^+ in each of the three compounds. Ebsworth and coworkers observe this ion (as well as Ge_3^+) in the mass spectrum of $(\text{GeH}_3)_3\text{P}$.⁴⁵ This ion is indeed real and is apparently formed in the fragmentation of the parent specie. The presence of the ion, he suggests, implies a ready redistribution of the bonding electrons. A similar case exists in regard to $\text{GeH}_3\text{CH}_2\text{SiH}_2\text{Cl}$,

where the ion GeSi^+ appears,¹¹⁵ and $(\text{SiH}_3)_2\text{CH}_2$, where Si_2^+ is present.⁸ This would also explain the appearance of Ge_2^+ in $(\text{GeH}_3)_2\text{CH}_2$ ⁵³ and $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$.

The intensity of Ge_2^+ in 1,1-digermylethane seems too great to arise only from easy redistribution of bonding electrons. The thermal instability of the compound suggests the probability that the Ge_2^+ is due more to decomposition of $(\text{GeH}_3)_2\text{CHCH}_3$ into digermane. Another possibility, of course, is that two Ge^+ fragments recombine in the spectrum to form the Ge_2^+ species. No matter how the Ge_2^+ ions arise, it is interesting to note that their presence is indeed a general occurrence in various digermyl derivatives.

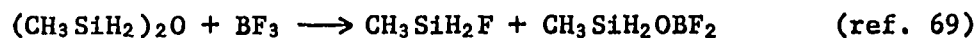
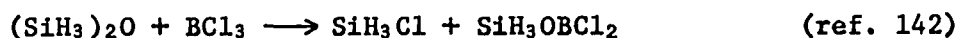
From Table III-5, it may be seen that the loss of a germyl group is more predominant in the case of $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ than in $(\text{GeH}_3)_2\text{CHCH}_3$. Apparently, the ion GeC_2^+ is more stable than the ion GeC^+ . The non-appearance of a GeC^+ ion in the $\text{GeH}_3\text{CH}_2\text{CH}_2\text{GeH}_3$ spectrum is to some extent expected from the relative bond strengths of Ge-C and C-C (51 and 83 kcal/mole, respectively).⁴³

B. The Reaction of Phosphorus Pentafluoride with Selected Silicon Hydrides

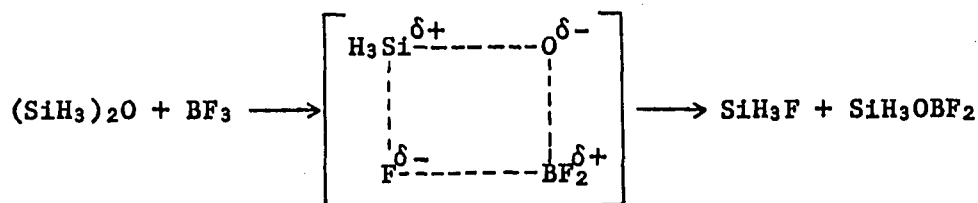
1. Previous Investigations

The interaction of Lewis acids with carbon, silicon and germanium ethers and amines has been thoroughly investigated by many groups of workers.^{33,69,84,89,90,92,135,137,142,170,205} Ethers and amines tend to act as Lewis bases by virtue of their ability to "donate" their lone pairs of electrons to appropriate Lewis acids. The final products observed in these interactions depend to a large extent on the type of

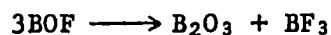
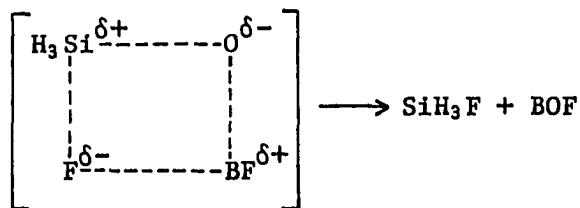
ether or amine undergoing reaction. For example, reactions of the typical Lewis acids BCl_3 and BF_3 with alkyl ethers and alkyl amines result in the formation of the expected 1:1 adducts,³³ while silicon ethers and amines readily undergo Si-O and Si-N bond cleavage reactions to yield silyl halides plus siloxyboron or silazaboron dihalides.^{35,69} 142,186,197 Germanium ethers have not been extensively investigated. From the data now available, it appears that they interact with boron trihalides to form either a simple adduct or to undergo cleavage as in the analogous silicon systems.⁹² Summarized below are some of the reactions of boron trihalides with carbon, silicon and germanium ethers:



The mechanism proposed by Emeleus and Onyszchuk for cleavage of the silicon-oxygen bond of siloxanes by BCl_3 or BF_3 involves two stages each stage going through a four-center cyclic transition state:^{69,142}

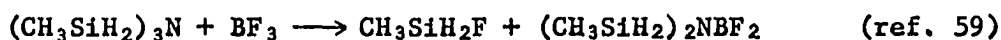
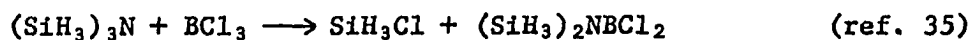


The SiH_3OBF_2 undergoes further decomposition which was also proposed as going through a four-center intermediate:



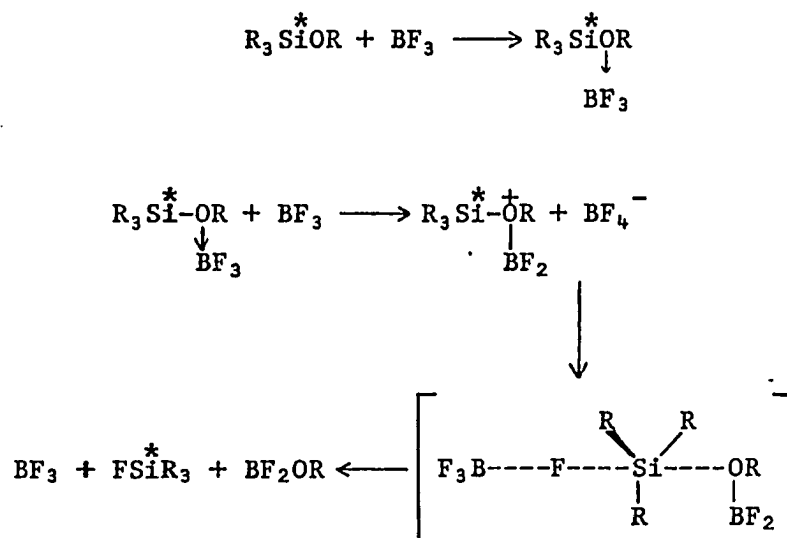
In addition, this general reaction sequence has been suggested for the boron halide cleavage of alkoxy silanes.

A simple four-center mechanism is also a possibility for the cleavage of silyl amines by the boron trihalides:^{35,59,186}



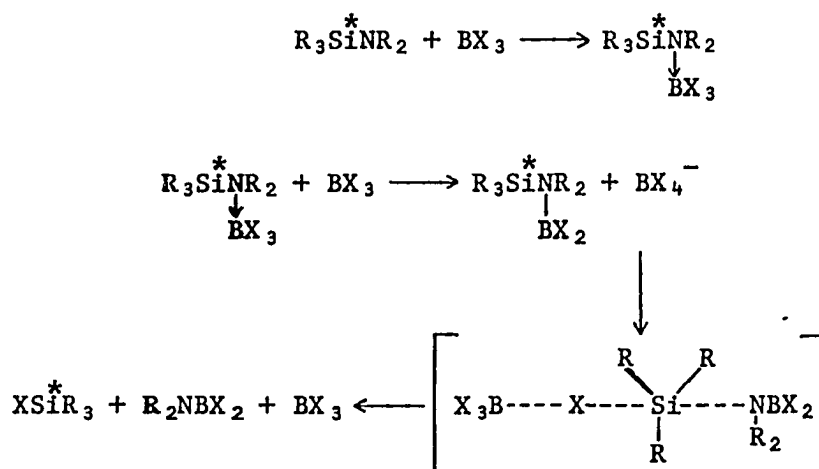
In the interaction of trisilylamine with BF_3 there is evidence of the formation of a borazole derivative from the further decomposition of $(\text{SiH}_3)_2\text{NBF}_3$.¹⁸⁶

However, the reaction sequence for all of the cleavages discussed above may be more complex than this simple four-center mechanism. This is based on the results of recent studies by Sommer, et al., on the cleavage of optically active alkoxy silanes and silylamines.¹⁷⁸ If the above mechanism is correct, optically active alkoxy silanes would lead to retention of configuration for the organohalosilane which is formed. This indeed is the case for BCl_3 cleavages. It is interesting to note, however, that the analogous BF_3 cleavages result in inversion of configuration. The mechanism proposed for the BF_3 cleavage of alkoxy silanes involves an $\text{S}_{\text{N}}2$ -Si attack of a fluoride ion (or complexed fluoride ion) at the rear of silicon displacing the alkoxy group:

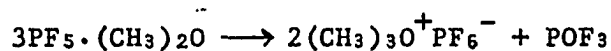


The difference in mechanism may be due in some degree to the stronger Lewis acidity of BCl_3 relative to BF_3 . The silicon-oxygen bond should thus be weaker when coordinated with BCl_3 than with BF_3 and should make silicon accept a chloride ion in the four-center mechanism better than a fluoride ion. However, these studies of alkyl-substituted silanes may not apply to the silicon hydrides investigated in this thesis.

Studies of boron halide cleavages of optically active silyl amines have shown that both BCl_3 and BF_3 cleave with inversion of configuration.¹⁷⁸ The proposed reaction sequence for these systems has been formulated as shown below:



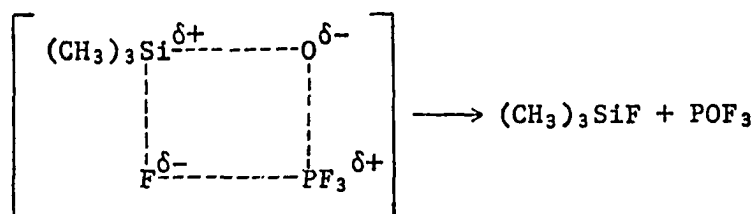
Many investigations have been conducted concerning the interactions of phosphorus pentafluoride with various Lewis bases.^{84,88,89,90,116,135,170} Organic ethers^{88,89} and amines^{135,170} generally form 1:1 adducts with PF₅, although Goodrich and Treichel have characterized adducts that contain a greater amount of phosphorus pentafluoride;⁸⁴



In reacting a substituted phosphorus fluoride with hexamethyldi-siloxane, Schmutzler obtained cleavage of the Si-O bond¹⁶⁹



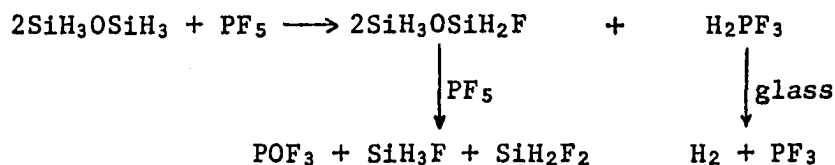
Kifer has found that a similar reaction occurs between $[(\text{CH}_3)_3\text{Si}]_2\text{O}$ and PF₅, producing (CH₃)₃SiF and POF₃:



The analogous cleavage reaction of phosphorus pentafluoride with the parent siloxane, (SiH₃)₂O, would be:



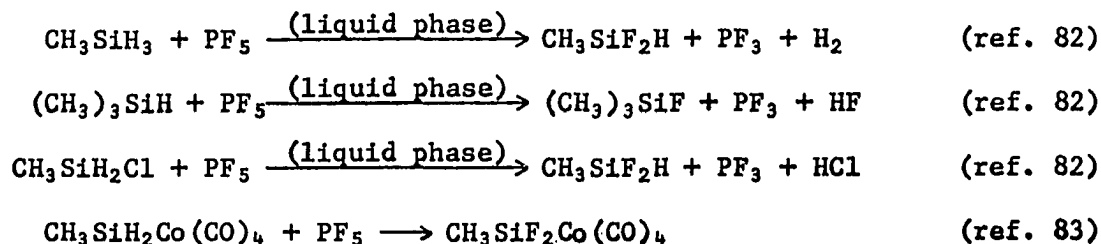
However, while attempting to study this latter reaction, Kifer observed the formation of partially fluorinated siloxanes in addition to SiH₃F and SiH₂F₂, especially when the reaction was carried out at low temperature (-78°).¹¹⁵ The proposed reaction scheme that accounts for the products is given as:



The partially fluorinated dimethyl compound, $\text{CH}_3\text{SiH}_2\text{OSiH}(\text{F})\text{CH}_3$, was also prepared by a similar reaction at -78° .¹¹⁵

It was concluded that overall, cleavage of the Si-O and Si-H bonds are competitive, with cleavage of Si-O predominating at room temperature, diminishing relative to Si-H cleavage with decreasing temperature and increasing with longer reaction times.

The fluorination of the Si-H bond by PF_5 has also been reported in certain other organosilicon hydrides. However, most of the work has been of a qualitative nature, rather than for preparative work. Some illustrations of the work are given below:



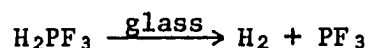
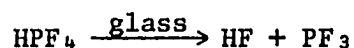
2. The Investigated Reactions

a. Fluorosilylpropenes

(1) Synthesis

The preparation of various fluorinated organosilanes was initiated by studying the 1:1 interaction between phosphorus pentafluoride and 3-silylpropene (allylsilane). The reaction yielded the expected products, viz., PF_3 , $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ and $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$ in addition to small amounts of SiH_3F and SiH_2F_2 , all of which were identified by their infrared and mass spectra. Monofluorosilane undoubtedly results from the cleavage by PF_5 of the Si-C bond in 3-silylpropane, while further cleavage of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ would be the source of difluorosilane. Phosphorus trifluoride (and hydrogen gas, observed upon opening the reaction vessel to the vacuum line) are products of the known

decomposition of HPF_4 and/or H_2PF_3 in the presence of glass:^{99,189}



No SiHF_3 was detected among the products. This is most likely due to the low concentration of $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$ available for further cleavage by PF_5 . Presumably an increased amount of difluorosilylpropene could have been obtained by increasing the amount of PF_5 relative to silylpropene. One would expect, in the latter case, to observe the presence of SiHF_3 as another cleavage product.

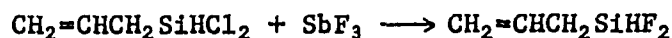
Preliminary vacuum line distillation of the products produced a mixture of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$, $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$ and unreacted $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$ which condensed in a -116° trap. The difference in molecular weight of the three products was only a maximum of 36 and of the two fluorinated compounds, only 18. Purification of the mixture could only be accomplished by gas chromatography using an 18 foot column. The yield of $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ was 60% and that of $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$ was 6%.

A sample of monofluorosilylpropene purified by gas chromatography and taken directly to the mass spectrometer produced a mass spectrum which contained a single "parent minus one hydrogen" peak corresponding to $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$. However, a sample allowed to warm to room temperature (in order to obtain an infrared spectrum, for example) furnished a mass spectrum containing three peaks which corresponded to the mono-, di- and trifluorosilylpropenes. The conclusion was reached that $\text{CH}_2=\text{CHCH}_2\text{SiF}_3$ did not originate by the direct interaction of allylsilane or other partially fluorinated allylsilane with phosphorus pentafluoride, but by the disproportionation of $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$:



It should be noted that the fluorination of 3-silylpropene resulted in a measurable amount of the difluoro compound, whereas Kifer found that no additional fluorination occurred on silicon after $(\text{SiH}_2\text{F})_2\text{O}$ had been formed, no matter what $\text{PF}_5:(\text{SiH}_3)_2\text{O}$ reaction ratio was used. It appears that if there is more than one electronegative group on silicon, the PF_5 fluorination reaction will not take place. For example, it is known that SiHCl_3 cannot be fluorinated by this method.¹¹⁵ This conclusion agrees with the proposed mechanism (section 2.d.). Thus $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$ can be converted to $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ and hence to $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$, but no additional fluorination occurs. In $(\text{SiH}_3)_2\text{O}$, one electronegative atom (oxygen) is already attached to silicon and thus only one additional fluorine can be introduced.

Difluorosilylpropene had been previously prepared by the reaction of antimony trifluoride with allyldichlorosilane:¹³⁴



Although the reaction of silylpropene with PF_5 was not attempting to prepare the difluoro compound, presumably the proper ratios of reactants would provide a convenient preparation of the latter compound. The method used in this research would eliminate the need to prepare the dichloro intermediate.

(2) Characterization

The proton magnetic resonance spectra of the silylpropenes are discussed in detail in section C.

Infrared spectra of the silylpropenes show many similarities. Table III-6 presents a comparison of selected absorptions for $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$, $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ and $\text{CH}_2=\text{CHCH}_2\text{SiHF}_2$. In this series of compounds, the successive substitution of the more electronegative

fluorine for hydrogen results in an increase in the Si-H stretching frequency. The withdrawal of electrons by fluorine increases the degree of s-character of the hydrogen-directed silicon orbital, resulting in a decrease in the Si-H bond distance and thus increasing the vibrational frequency.¹⁷⁶ The corresponding increase in the Si-H deformation frequency may also be due to a similar effect.

Table III-6
Comparison of Selected Absorption Frequencies
for Some Silylpropenes and Related Compounds

	$\nu(\text{SiH})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}-\text{C})$	$\nu(\text{Si}-\text{F})$	$\delta(\text{SiH})$	$\nu(\text{Si}-\text{C})$
$\text{CH}_2=\text{CHCH}_2\text{SiH}_3^{\text{a}}$	2150	1623	1038	--	925	590
$\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}^{\text{a}}$	2194	1639 1632	1042	975 970 963	936 927	599
$\text{CH}_2=\text{CHCH}_2\text{SiHF}_2^{\text{a}}$	2230	1633	1030	973,900	955 945	593
$\text{SiH}_3\text{F}^{\text{b}}$	2206 2196	--	--	872	990,943	--
$\text{SiH}_2\text{F}_2^{\text{c}}$	2250 2246	--	--	982,870	--	--
$\text{CH}_2=\text{CHCH}_2\text{Br}^{\text{d}}$	--	1638	924	--	--	--

^a Recorded during the present research.

^c Reference 46.

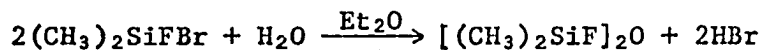
^b Reference 140.

^d Reference 94.

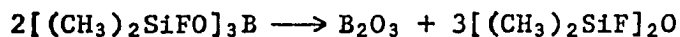
The other observed stretching vibrations occur in the expected regions of the spectrum, i.e., C=C, 1632-1639; C-C, 1030-1042; Si-F, 927-955; and Si-C, 593-599.

b. Fluorosiloxanes

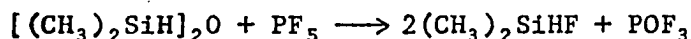
1,1'-Difluoro-1,1,1',1'-tetramethyldisiloxane has been previously prepared by the hydrolysis of $(\text{CH}_3)_2\text{SiFBr}$ with water in ether⁷¹



and by thermal disproportionation of tris(dimethylfluorosiloxy)borane.¹³³



However, neither of these two intermediates is readily available. Since $[(\text{CH}_3)_2\text{SiH}]_2\text{O}$ is readily available (either by a chemical synthesis or purchase from Peninsular), it seemed desirable to investigate the synthesis of $[(\text{CH}_3)_2\text{SiF}]_2\text{O}$ by the interaction of the hydrosiloxane with phosphorus pentafluoride. In the present work, PF_5 and $[(\text{CH}_3)_2\text{SiH}]_2\text{O}$ were allowed to react in a 2:1 ratio. After maintaining the reaction mixture at room temperature for 15 minutes, the only products were PF_3 , POF_3 , $(\text{CH}_3)_2\text{SiHF}$ and $(\text{CH}_3)_2\text{SiF}_2$. The last three compounds undoubtedly resulted from a Si-O-Si bond cleavage reaction of the siloxanes $[(\text{CH}_3)_2\text{SiH}]_2\text{O}$ and $[(\text{CH}_3)_2\text{SiF}]_2\text{O}$ and perhaps $(\text{CH}_3)_2\text{SiHOSiF}(\text{CH}_3)_2$ as discussed previously:



Phosphorus trifluoride results, as mentioned earlier, from the decomposition of HPF_4 or H_2PF_3 in the presence of glass. The latter compounds indicate that a Si-H bond has been fluorinated, as does the presence of $(\text{CH}_3)_2\text{SiF}_2$.

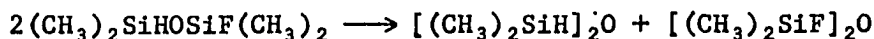
Since it appears that $(\text{CH}_3)_2\text{SiHOSiF}(\text{CH}_3)_2$ and $[(\text{CH}_3)_2\text{SiF}]_2\text{O}$ may have been formed in the reaction but underwent cleavage under room temperature conditions, a similar reaction between $[(\text{CH}_3)_2\text{SiH}]_2\text{O}$ and PF_5 was carried out for 20 minutes. Under these conditions, the reaction

gave a greater than 50% yield of $[(\text{CH}_3)_2\text{SiF}]_2\text{O}$. This method of complete fluorination is preferable to other methods investigated owing to the minimum number of intermediates that are involved. Also, the synthetic procedure can be easily performed in a relatively short period of time.

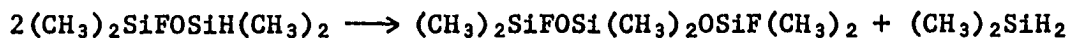
A reaction mixture composed of PF_5 and $[(\text{CH}_3)_2\text{SiH}]_2\text{O}$ in a 1:1 ratio at room temperature yielded the same cleavage products as mentioned above. A similar reaction mixture allowed to interact at -96° for 4 minutes also contained the cleavage products; however, phosphorus trifluoride was also formed. This was a good indication that the fluorination of the Si-H bond had occurred. A gas chromatographic separation of the reaction products did not yield a peak which could be assigned to the monofluoro compound. The only fluorosilane that could be detected was $[(\text{CH}_3)_2\text{SiF}]_2\text{O}$.

Evidence for the formation of the monofluoro compound is given below. A mass spectrum of the products revealed the uppermost peaks to have a m/e value of 151 and 155. A precise mass measurement of the peak at 155 corresponds to the ion $[(\text{CH}_3)_2\text{SiFOSiF}(\text{CH}_3)]^+$, which can only originate from the loss of a methyl group from $[(\text{CH}_3)_2\text{SiF}]_2\text{O}$. The peak at 151 corresponds to the ion $[(\text{CH}_3)_2\text{SiOSiF}(\text{CH}_3)_2]^+$, which can arise from either the "parent minus one hydrogen" ion of $(\text{CH}_3)_2\text{SiHOSiF}(\text{CH}_3)_2$ or from the loss of a fluorine from the difluoro compound. A mass spectrum of a pure sample of the latter compound disclosed an absence of the 151 peak in the fragmentation pattern. The 151 ion, therefore, must only originate from the monofluoro-tetramethyldisiloxane. The absence of this compound in the gas chromatography procedure leads to the conclusion that the compound may be thermally unstable (detector temperature was 85°) and might have

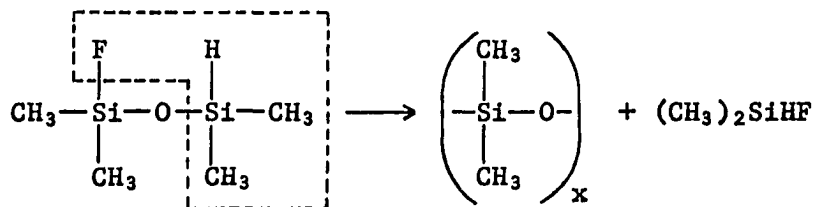
disproportionated according to the equation:



In an attempt to determine the gas phase molecular weight of a vacuum line-purified sample of the reaction products from the 1:1 reaction, it was noticed that while the first determination was reasonably close to the calculated value (meas., 151.6, calc. 152.28),²⁰ successive determinations exhibited a continual decrease. In addition, a white solid appeared on the walls of the vacuum line cold finger. Decomposition at room temperature to yield a polymer plus a lower molecular weight gas, e.g. $(\text{CH}_3)_2\text{SiH}_2$, could account for the observations. Such a reaction might proceed as follows:



Another possible reaction that would account for the solid polymer formation involves the elimination of $(\text{CH}_3)_2\text{SiHF}$ from the monofluoro-disiloxane, i.e.



It is not entirely clear why monofluorotetramethyldisiloxane would be unstable once formed. Kifer found marginal evidence for the disproportionation of $\text{SiH}_3\text{OSiH}_2\text{F}$ occurring if the sample was impure. The presence of methyl groups attached to the silicon atoms may increase this tendency to disproportionate in the presence of impurities.

c. Fluorosilylamines

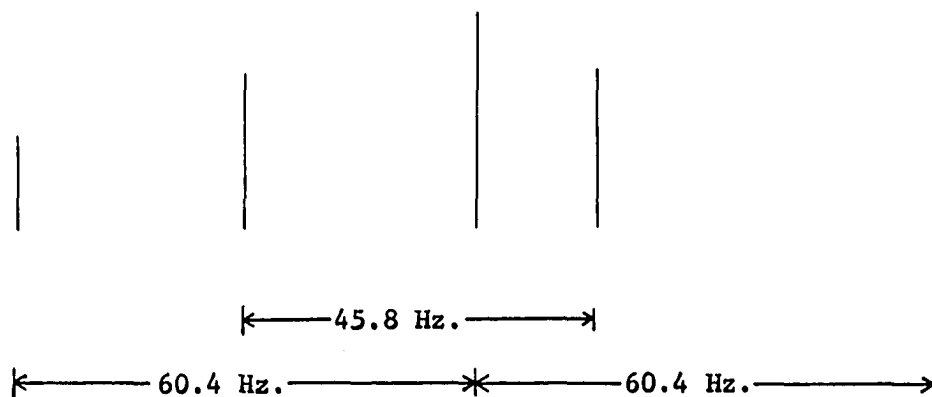
(1) Synthesis

Having shown that fluorine atoms can be introduced into hydrosiloxanes by the phosphorus pentafluoride method, one of the goals of the present research project was to investigate the fluorination of hydrosilylamines by this method. When $[(\text{CH}_3)_2\text{SiH}]_2\text{NH}$ and PF_5 were allowed to interact in a 1:1 ratio at -45° and -78° , the volatile products were $(\text{CH}_3)_2\text{SiHF}$, $(\text{CH}_3)_2\text{SiF}_2$ and PF_3 . The appearance of PF_3 and $(\text{CH}_3)_2\text{SiF}_2$ is evidence of the formation of the fluorinated amine, which appears to be less stable than the analogous disiloxane, for there is no trace of the fluorinated disilylamine in the mass spectrum of the products. The reasons for the instability of the compound are also unclear.

The reaction of phosphorus pentafluoride with trisilylamine resulted in evidence for the formation of mono-, di- and trifluoro-trisilylamine. Reaction mixtures containing up to a six-fold excess of PF_5 resulted in the formation of mainly $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$.

Various ratios of $\text{PF}_5:(\text{SiH}_3)_3\text{N}$ were sealed in nmr tubes in order to qualitatively observe the possible course of the reaction. The ratios and their reaction times were: (1) - 6:1, 2.25 hours, (2) - 3:1, 1.75 hours, (3) - 1:1, 2.5 hours. The spectra were recorded at concentrations of 25 v/v% in cyclopentane and at a temperature of -1° controlled by a Varian Variable Temperature accessory to the HA-100.

The final spectrum for reactions (1) and (2) were identical, consisting of a five line pattern. The spectrum was actually a doublet ($J = 45.8 \text{ Hz.}$) and a triplet ($J = 60.4 \text{ Hz.}$).



The absorptions correspond to SiH_3F ($\delta_{\text{H}} = 5.24\tau$, $J_{\text{HF}} = 45.8 \text{ Hz.}$) and SiH_2F_2 ($\delta_{\text{H}} = 5.29\tau$, $J_{\text{HF}} = 60.5 \text{ Hz.}$).^{64,65} Thus, the two reactions initiated with excess PF_5 conclude after several hours with only cleavage products present.

Figure III-A shows spectra recorded from reaction (1) as a function of time. The spectra were started at the following times after insertion of the sample into the spectrometer (the spectrometer was run at a scan speed of 500 seconds/250 Hz.):

spectrum A -- 1 minute
 spectrum B -- 5 minutes
 spectrum C -- 8 minutes
 spectrum D -- 26 minutes
 spectrum E -- 48 minutes
 spectrum F -- 130 minutes

In spectrum A, it was noticed that shortly after commencement of the reaction, a large peak occurred downfield from trisilylamine (TSA) at 5.55τ . This peak has not been assigned. It was first considered as arising from the SiH_3 protons in $(\text{SiH}_3)_2\text{NSiH}_2\text{F}$, but was not assigned as such due to the ratios of the measured areas under the 4.97τ and 5.55τ peaks. The expected ratio is 1:6, but the measured ratio is 1:7.8 in

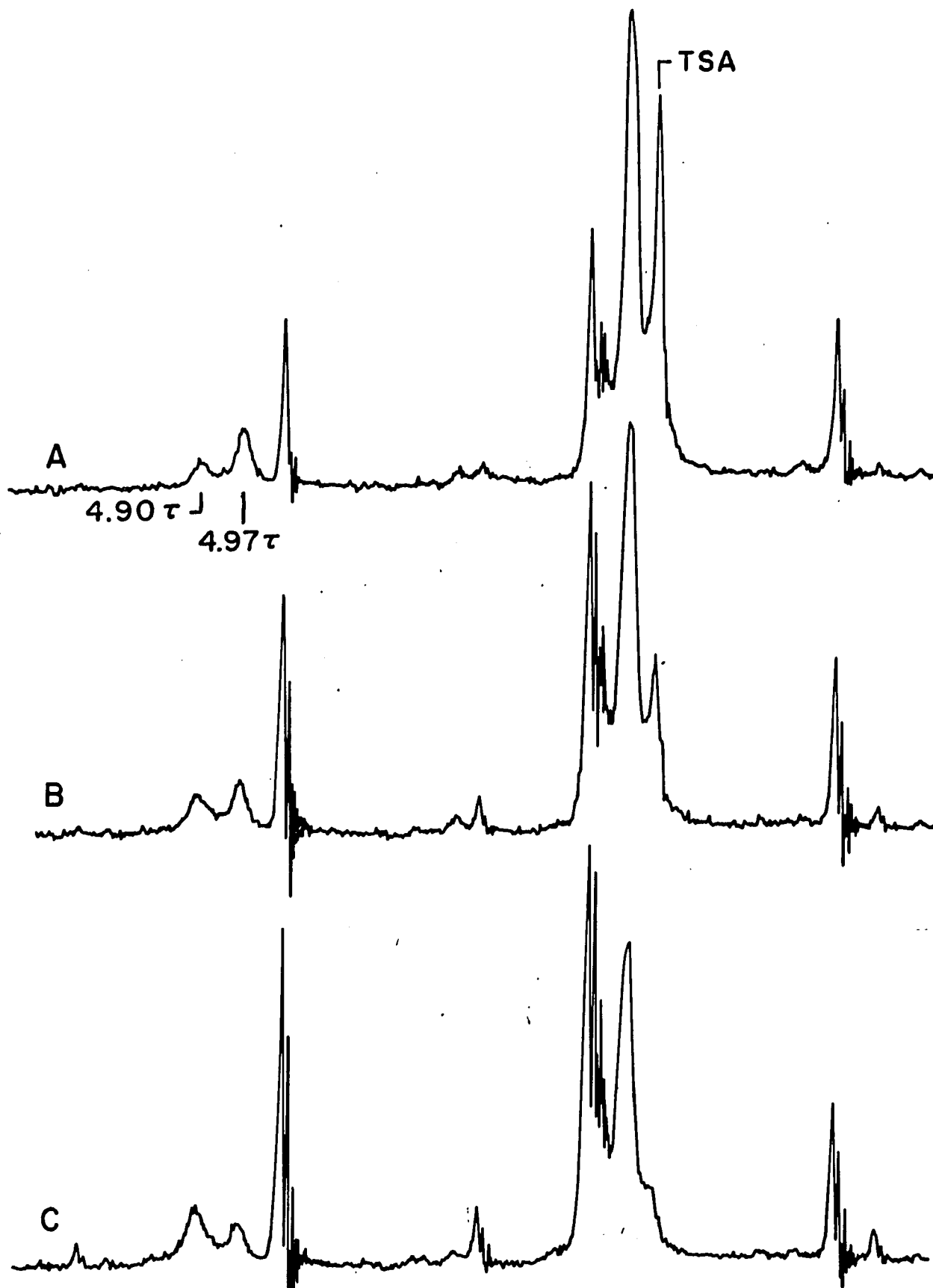


Figure III-A The Progress of the Reaction of PF_5 and $(\text{SiH}_3)_3\text{N}$ as Observed by Proton Magnetic Resonance

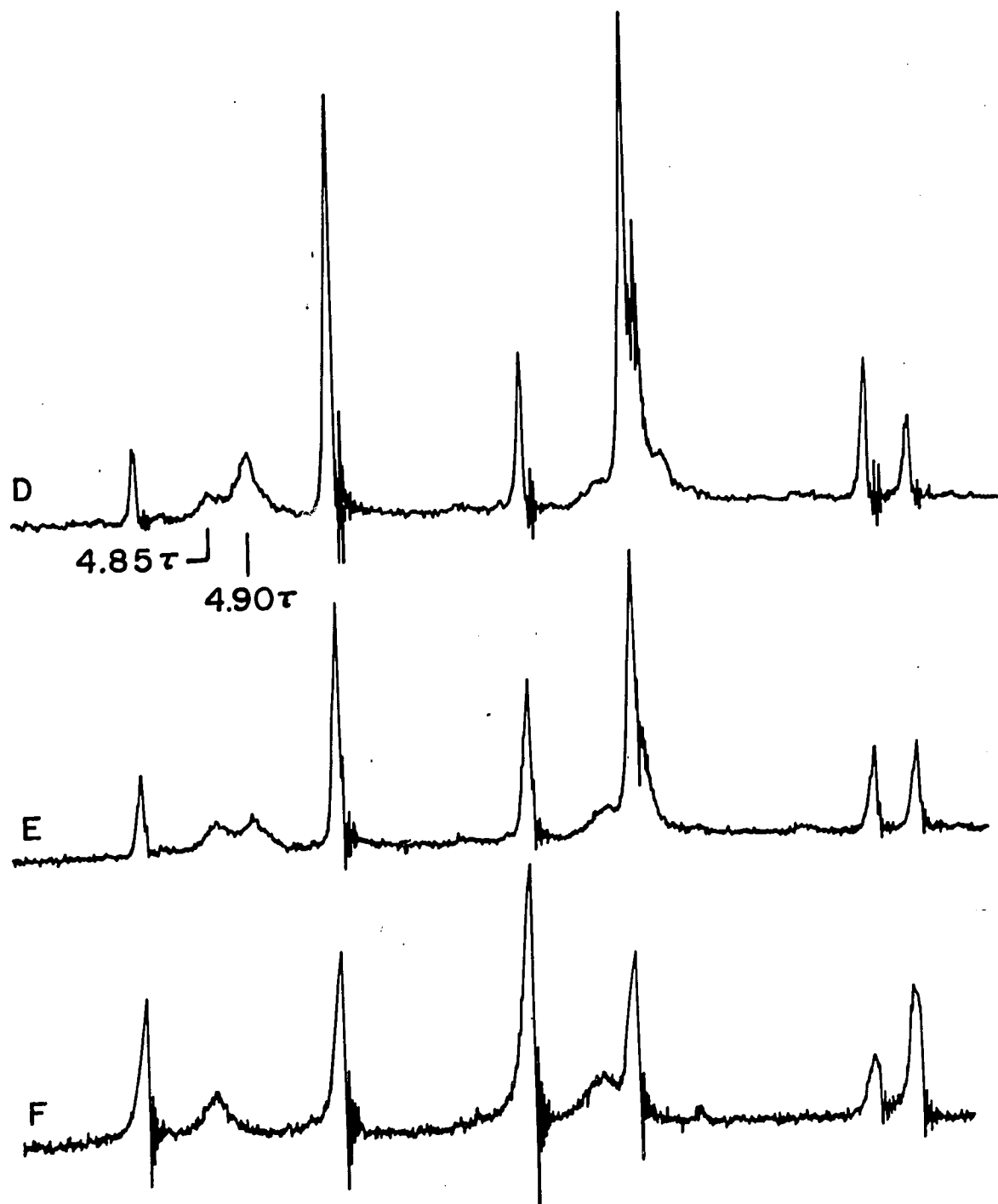


Figure III-A - (continued)

spectrum A, 1:7.5 in spectrum B and 1:6.8 in spectrum C. As can be seen, the two peaks even diminish unequally. Furthermore, the SiH_3 protons should exhibit long range coupling with the fluorine on SiH_2F . The peak at 5.55τ does not have any evidence of this coupling. A doublet corresponding to SiH_3F (5.24τ) appeared at the same time as the 5.55τ singlet. The small, relatively broad peak which occurred at 4.97τ was interpreted as being the downfield portion of the doublet resulting from $J_{\text{H}'-\text{F}}$ in $(\text{SiH}_3)_2\text{NSiH}_2'\text{F}$, the upfield portion being obscured by the right-hand member of the SiH_3F doublet and by the singlet at 5.55τ . Also obscured was the absorption due to the $(\text{SiH}_3)_2$ protons.

As the reaction proceeded, the SiH_3F doublet increased rapidly while the TSA singlet decreased rapidly. The SiH_2F_2 triplet appeared and also increased (spectra B, C). The peak corresponding to the monofluoro compound increased only slightly. Furthermore, a second broad peak appeared downfield (4.90τ , spectrum A) from the first. This second peak corresponded to the downfield portion of $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$ (Figure II-V). The upfield portion and the triplet were also obscured in spectra A-C by the right-hand member of the SiH_3F doublet. The difluoro peak attained a steady state while the first peak (monofluoro) diminished (spectra B, C) until it completely disappeared (spectrum D).

About 25 minutes after the reaction commencement, a third peak appeared downfield from the first two (spectrum D). Its τ value (4.85) matched the downfield peak in the $(\text{SiH}_3\text{F})_3\text{N}$ spectrum (Figure II-V) and this time the upfield peak was not obscured. The chemical shift and coupling constant corresponded to the values determined for the pure compound in this research work (Table II-37). The trifluoro compound attained a steady state and the difluoro peak diminished (spectrum E).

During this period, the SiH_3F doublet had been slowly decreasing and the SiH_2F_2 triplet slowly increasing so that by the time spectrum F was reached the SiH_3F and SiH_2F_2 peaks were about equal in intensity and there was a small amount of $(\text{SiH}_2\text{F})_3\text{N}$ present.

Reaction (2) started similarly, though after an hour and a half only a trace amount of SiH_2F_2 was present. No trifluorotrisilylamine was observed. The only peaks present represented SiH_3F and equal amounts of the mono- and difluoro amines. After several days at room temperature, only SiH_3F and SiH_2F_2 were observed.

Reaction (3) was slower, as expected, and did not go as far to completion as (1) and (2). After 2.5 hours, the difluorotrisilylamine peak was still only half as intense as the monofluoro and very little SiH_2F_2 was present.

Mass spectral data yielded conclusions about the reaction which were similar to those obtained from nmr evidence. The products of a 1:1 $\text{PF}_5:(\text{SiH}_3)_3\text{N}$ reaction performed in a breakseal tube (after vacuum line distillation to remove cleavage products) showed mass peaks at 124 and 142 corresponding to the "parent minus one hydrogen" of mono- and difluorotrisilylamine, with the 124 peak being of greater intensity. A 3:1 reaction contained the identical peaks, this time the 142 peak having a greater intensity. In addition, a peak of low intensity was present at 160 (trifluoro compound). A 6:1 reaction gave products with an intense 160 peak (trifluorotrisilylamine) plus a low intensity peak at 142 (difluorotrisilylamine).

With the encouraging qualitative results discussed, a project was planned to try to prepare and separate these compounds. Several reactions with varying ratios of $\text{PF}_5:(\text{SiH}_3)_3\text{N}$ (1:1, 3:1, 6:1) were

sealed in breakseal tubes and allowed to react at various temperatures (-96° to 0°) for 20 minutes. Temperatures lower than -50° seemed to prevent the reaction from occurring at all, while temperatures above -23° yielded only PF_3 , SiH_3F and SiH_2F_2 . In the range -50° to -23° , in addition to these products, mono-, di- and trifluorotrisilylamine were detected mass spectrally, in varying proportions depending on the initial reaction ratios of phosphorus pentafluoride and trisilylamine. Preliminary fractionation in the vacuum line separated the three fluorosilylamines (in a -96° trap) from cleavage products. Attempted further purification by gas chromatography resulted only in decomposition, even when the glass column (col. H) was used. Satisfactory purification was finally achieved by using the low-pressure fractionating column (Figure II-B). The most abundant fluorosilylamine was $\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$ and thus this product was the one which was most completely characterized.

(2) Characterization

The proton magnetic resonance data for the three fluorosilylamines and some related compounds are summarized in Table III-7. It is interesting to compare the chemical shifts of these amines with the corresponding fluorosilylethers. In the latter compounds, substitution of a fluorine for a hydrogen on silicon causes only a slight shift in the resonance of the remaining SiH_2 protons towards lower field but causes a large shift downfield for the SiH_3 resonance.¹⁹⁶ This is somewhat unusual since the SiH_3 group is on the other end of the molecule. In the pmr spectra of the silylamines, however, there is a notable difference. There is a trend for the SiH_2 proton resonance to decrease as successive fluorine substitution on the

Table III-7
Proton Magnetic Resonance Data for Fluorinated Trisilylamines
and Related Compounds

Compound	τSiH_3	τSiH_2	J_{HF}^{a} (adjacent)	J_{HF}^{a} (long range)
$\text{SiH}_3\text{F}^{\text{b}}$	5.24	--	45.8	--
$\text{SiH}_2\text{F}_2^{\text{b}}$	--	5.29	60.5	--
$(\text{SiH}_3)_3\text{N}^{\text{b}}$	5.56	--	--	--
$(\text{SiH}_3)_2\text{NSiH}_2\text{F}$	d	5.27 ^c	60.3 ^c	d
$\text{SiH}_3\text{N}(\text{SiH}_2\text{F})_2$	5.59	5.20	60.3	1.52
$(\text{SiH}_2\text{F})_3\text{N}$	--	5.15	60.3	d
$(\text{SiH}_3)_2\text{O}^{\text{e}}$	5.39	--	--	--
$\text{SiH}_3\text{OSiH}_2\text{F}^{\text{f}}$	5.28	5.36	61.2	--
$(\text{SiH}_2\text{F})_2\text{O}^{\text{f}}$	--	5.25	61.2	--

^a Values reported in Hz.	^d Not observed.
^b References 64 and 65.	^e Reference 65.
^c Values obtained as described in text.	^f Reference 196.

three silyl groups is achieved (see Table III-7). As can be noted from the table, the SiH_3 proton resonance of $(\text{SiH}_3)_3\text{N}$ shifts to higher field when two fluorine atoms are substituted into the molecule.

In fluorinated silanes, the H-F coupling constants are known to be sensitive to the number of electronegative substituents on the silicon. For example, in SiH_3F , $J_{\text{HF}} = 45.8$ Hz.; in SiH_2F_2 , $J_{\text{HF}} = 60.5$ Hz.; in SiHF_3 , $J_{\text{HF}} = 96.3$ Hz. In the present fluorosilylamines, this coupling was found to be 60.3 Hz. This value is consistent with two electronegative

groups about silicon; in the present case, they are fluorine and nitrogen. This is further proof that in the fluorosilylamine preparation, not more than one fluorine is on each silicon.

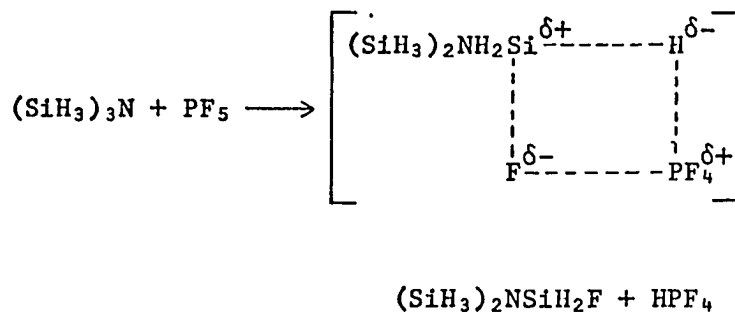
The coupling constants of $\text{SiH}_3\text{N}(\overline{\text{SiH}_2\text{F}})_2$ and $(\overline{\text{SiH}_2\text{F}})_3\text{N}$ turn out to be exactly equivalent. Since a spectrum of a pure sample of $(\text{SiH}_3)_2\text{NSiH}_2\text{F}$ could not be obtained, it was assumed that the $\text{H}_2\text{Si-F}$ coupling constant of this compound would be identical to the other two (60.3 Hz.). The chemical shift of the monofluoro compound was determined by adding 30.15 Hz. (i.e., half of 60.3 Hz.) to the peak observed in Figure III-A which had been assigned to $(\text{SiH}_3)_2\text{NSiH}_2\text{F}$ (i.e. 4.97τ). The value obtained by this addition (5.27τ) is the value listed in Tables II-41 and III-7. The broadness of the proton magnetic resonance spectrum of $(\text{SiH}_2\text{F})_3\text{N}$ (Figure II-V) may be due to unresolved long range splitting between fluorine and SiH_2 protons.

The mass spectra of the three fluorosilylamines show no unusual features. It is interesting to note that in the parent ion region, the most intense peak is the "parent minus one hydrogen". The parent ion peak is much less intense compared to the "parent minus one" peak. This is perhaps due to the hydridic nature of the Si-H bond.

d. Mechanism

The mechanism for the fluorination by phosphorus pentafluoride has not been established. A look at some related fluorinations by PF_5 may provide helpful information. The PF_5 fluorination of such compounds as $\text{CH}_3\text{SiH}_2\text{Cl}$ and $\text{CH}_3\text{SiH}_2\text{Co}(\text{CO})_4$ (page 153) proceed at room temperature.⁸² Ethyl- and vinylsilane were fluorinated at around 0° .⁷² The silylamines discussed in the present work required much lower temperatures than other compounds which have been fluorinated by this method. Noting that the

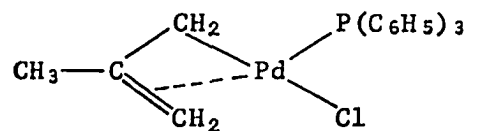
tendency to fluorinate the Si-H bond increases in the series $\text{Cl}_3\text{SiH} < \text{CH}_3\text{SiH}_2 < (\text{CH}_3)_3\text{SiH}$, it has been suggested that the rate controlling step may involve an electrophilic attack of a Si-H bond by phosphorus:



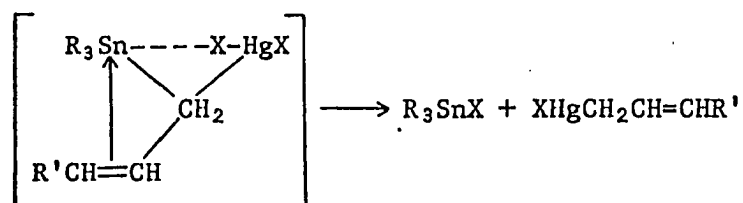
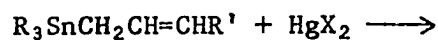
Thus any group on silicon that promotes the $\text{Si}^{\delta+}-\text{H}^{\delta-}$ charge separation (such as methyl) will promote the fluorination reaction. Likewise, any group that promotes $\text{Si}^{\delta-}-\text{H}^{\delta+}$ (such as oxygen or nitrogen) will decrease the fluorination products.

C. The High Resolution Proton Magnetic Resonance Study of Allylic Derivatives of Group IVB Elements

It is well known that for certain allyl transition metal complexes, the double bond of the σ -bound allyl group interacts with the transition metal as illustrated:¹³²

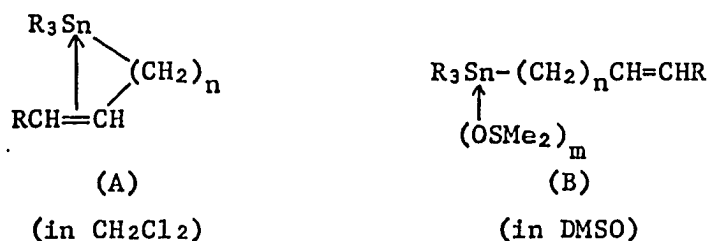


This type of interaction between low-lying d orbitals and p_π olefinic orbitals has also been proposed as a cyclic intermediate in the reaction of certain allyl tin compounds with mercuric halides:¹⁵⁴



Some infrared, Raman and ultraviolet spectral studies of similar compounds have also yielded data which favor the presence of this type of interaction.¹⁵²

However, the results of an infrared and pmr study have not been in accord with the presence of this type of overlap. Using the fact that silver-olefin π complexes have a $\nu(C=C) \sim 55-70 \text{ cm}^{-1}$ lower than the free olefin,¹⁴⁸ Clark and Poller recorded the infrared spectra of several allylic derivatives of tin in methylene chloride and dimethylsulfoxide (DMSO).⁴¹

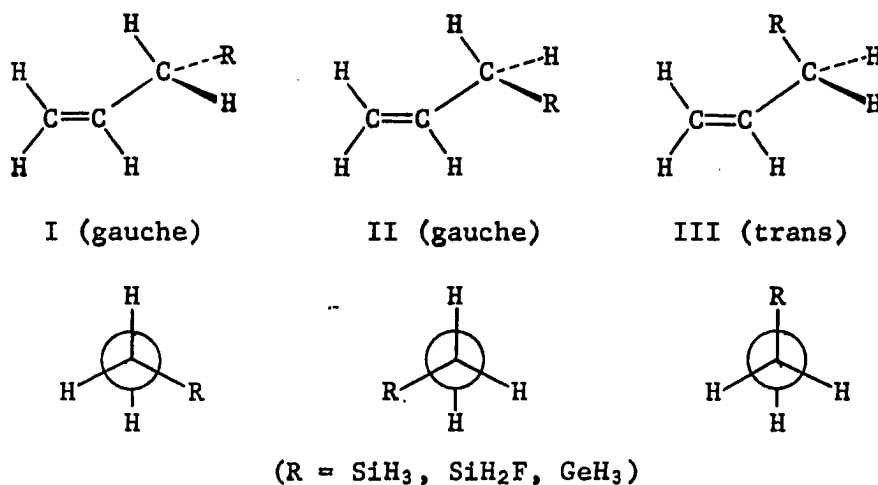


If the p-d overlap occurred (A), it would be detectable in the methylene chloride solution but greatly reduced in the DMSO. In the latter solvent, a solid complex forms,¹²⁴ decreasing to a great extent tin's acceptor strength (B). It was found that none of the $\nu(C=C)$ frequencies were lower for the methylene chloride solutions.

The nmr spectra of the above solutions were also reported. The chemical shift of the olefinic proton in an olefin π -complexed with silver is moved downfield from the free olefin.¹⁴⁰ One would expect, therefore, to see this effect in the above methylene chloride and DMSO solutions if π bonding were present. However, the observed shifts were small and in the opposite direction than expected. The authors conclude that these two results provide evidence against $(p \rightarrow d)\pi$ bonding in these molecules in the ground state.

It should be possible to detect this type of π -interaction by using pmr spectroscopy. In the present work, it was decided to investigate the effect in certain silicon and germanium hydrides. These were chosen because (1) the parent SiH_3 and GeH_3 derivatives could be investigated rather than the trialkyl or triaryl derivatives (where the effects of the organic grouping are unknown and would be expected to hinder this type of π -interaction) and (2) electronegative groups can be easily introduced on the silicon. Fluorine attached to silicon is known to lower the energy of silicon's d orbitals and possibly would cause them to be more involved in a π -type bonding than when fluorine is not present.

In essence, the object is to demonstrate whether conformer III contributes more than would be expected from free rotation.



In conformer III, the R group in the $\text{CH}_2=\text{CHCH}_2\text{R}$ compound is spatially adjacent to the double bond. Thus this conformer should predominate if there is an overlap of low-lying d and olefinic p_π orbitals.

In general, it has been shown that coupling constants for protons on adjacent trigonal (C_{III}) and tetrahedral (C_{IV}) carbon atoms ($J_{1,4}$ in these systems) are dependent on the $\text{H}-\text{C}_{\text{III}}-\text{C}_{\text{IV}}-\text{H}$ dihedral angle and can be approximated by the equation²⁵

$$J_{1,4}^0 = \frac{J_t + 2J_g}{3}$$

where J_t is the trans and J_g the gauche coupling constant. If the relative amounts of conformers I, II and III are $x:x:1$, the expression becomes²⁶

$$J_{1,4}^1 = \frac{xJ_t + (1+x)J_g}{1 + 2x}$$

If the molecule is entirely in the gauche conformation, the equation becomes

$$J_{1,4}^2 = \frac{1}{2}(J_t + J_g)$$

Bothner-By, et al., have obtained values of $J_t \approx 11.6$ Hz. and $J_g \approx 3.7$ Hz. from studies of substituted t-butylpropenes.²⁶ Substituting

these values in the above equation, one obtains $J_{1,4}^2 \approx 7.65$ Hz. The experimental values resulting from the LAOCN 3 analysis of the pmr spectra of group IVB substituted propenes are greater than 7.65 Hz. (Table III-8). Of course, it is not expected that all allyl systems would have J_t and J_g values identical with those found for t-butylpropenes. However, it still seems likely that the larger the value of $J_{1,4}$, the lower the number of conformers in the trans conformation. Interestingly, the fluorosilylpropene exhibits the same large $J_{1,4}$ as the nonfluorinated silane. Evidently the fluorine does not influence the olefinic protons to any appreciable extent.

Another equation can be derived to determine the percent of trans conformer. For allyl halides, Bothner-By, et al., have empirically arrived at the equation:²⁶

$$J_{1,4}^3 = -3 + 17 \cos^2 \phi$$

where ϕ is the dihedral angle. In I, II and III, $\phi = 180^\circ, 300^\circ, 60^\circ$.

If the amount of trans conformer is = n, then the gauche conformers have a population of (1-n). We thus obtain¹⁵⁶

$$J_{1,4}^3 = -3 + 17 \left[+ \frac{1}{2}(1-n) \cos^2 180^\circ + \frac{1}{2}(1-n) \cos^2 300^\circ + n \cos^2 60^\circ \right]$$

Solving for n, we get

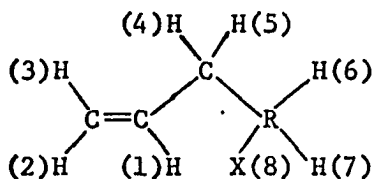
$$n = 1.2 - 0.16 J_{1,4}^3$$

Of course, this equation is derived for allyl halides and may not apply exactly to the group IVB derivatives, especially since $J_{1,4}^3 > 7.5$ Hz. results in $n = 0$. However, it does seem likely that the greater the values of $J_{1,4}$, the smaller the value of n. The result is the same as previously; the compounds have a low trans population.

Whipple, et al., have suggested that $J_{2,4}$ and $J_{3,4}$ are smaller when molecules are in conformations I and II.²⁰⁶ This has been confirmed by

Table III-8

Proton Magnetic Resonance Data for Several Substituted Propenes



	R=C, X=H ^a 10% in CCl ₄	R=Si, X=H 20% in CDCl ₃	R=Si, X=H 90% in CDCl ₃	R=Si, X=F 10% in CDCl ₃	R=Si, ^b X=H(6)=H(7) = C ₂ H ₅ 30% in CCl ₄	R=Ge, X=H 20% in CDCl ₃
<u>Chemical Shifts (τ)</u>						
w(1)	4.22	4.17	4.22	4.21	4.24	4.12
w(2)	5.13	5.10	5.13	4.96	5.27	5.15
w(3)	5.06	5.02	5.06	4.94	5.23	5.04
w(4)=w(5)	8.00	8.29	8.35	8.09	8.48	8.10
w(6)=w(7)	--	6.451	6.447	5.30	--	6.40
<u>Coupling Constants (Hz.)</u>						
J _{1,2}	10.3	10.1	10.1	10.2	9.2	10.1
J _{1,3}	17.2	16.9	16.9	17.0	17.3	17.0
J _{1,4} =J _{1,5}	6.2	7.7	7.7	7.8	7.8	8.0
J _{1,6} =J _{1,7}	--	-0.0	-0.0	-0.0	--	--
J _{1,8}	--	-0.0	-0.0	0.3	--	--
J _{2,3}	2.00	1.8	1.8	1.6	2.5	1.8
J _{2,4} =J _{2,5}	-1.3	-1.1	-1.0	-1.0	-1.3	-0.9
J _{2,6} =J _{2,7}	--	0.2	-0.0	0.0	--	--
J _{2,8}	--	0.2	-0.0	0.2	--	--
J _{3,4} =J _{3,5}	-1.7	-1.4	-1.5	-1.45	-0.9	-1.3
J _{3,6} =J _{3,7}	--	0.1	0.0	0.0	--	--
J _{3,8}	--	0.1	0.0	0.0	--	--
J _{4,6} =J _{4,7}	--	3.8	3.9	2.7	--	3.6
J _{4,8} =J _{5,8}	--	3.8	3.9	5.6	--	3.6
J _{6,8} =J _{7,8}	--	--	--	49.1	--	--
^a Reference 25			^b Reference 111			

Bothner-By²⁶ and the data obtained in this research (Table III-8) agree with the conclusions obtained considering $J_{1,4}$ coupling.

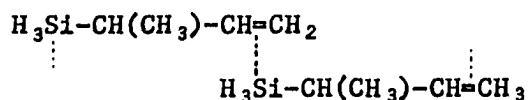
The sum of the coupling constants $J_{1,2}$, $J_{1,3}$ and $J_{2,3}$ (Σ_J) is known to be related to perturbation of the vinylic proton distribution. For example, the sums for trimethylvinylsilane and propene are $\Sigma_J = 38.8$ Hz.⁹⁸ and 29 Hz.,¹⁶⁸ respectively. The difference has been ascribed to p-d overlap between the adjacent silicon and carbon atoms.⁹⁸ It would be expected that this type of interaction between silicon and the p_π orbitals of the C=C double bond would give a similar result. Σ_J for 1-butene and the compounds prepared in this research show little variation (compound, Σ_J : $\text{CH}_2=\text{CHCH}_2\text{CH}_3$, 29.51; $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$, 28.75; $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$, 28.84; $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$, 28.97). Thus this result also lends no support to the presence of $(p \rightarrow d)\pi$ bonding in the ground state in the compounds investigated.

Several low temperature studies have been performed on various substituted propenes which indicate that $J_{1,4}$ would be expected to increase with decreasing temperature if the conformers are in conformation I and II, and conversely, to decrease with decreasing temperature if in conformation III. By using the variable temperature accessory with the HA-100, it was possible to obtain spectra of 3-monofluoro-silylpropene at -50° . $J_{1,4}$ was found to remain unchanged ($J_{1,4} = 7.81$ Hz.). Thus low-temperature studies do not shed any additional information about the mode of bonding in these compounds. Low temperature studies on $\text{Et}_3\text{SnCH}_2\text{CH}=\text{CHPh}$ also yield virtually unchanged coupling constants.¹¹¹

It is therefore concluded that the allylic compounds investigated in this research do not exhibit intramolecular $(p \rightarrow d)\pi$ bonding in the

ground state. Jones, et al., in an article published shortly after the research reported here was completed, in regard to a series of allylic derivatives of alkyl substituted group IVB elements, also arrives at this conclusion.¹¹¹ Perhaps steric interference of the bulky substituent (SiH_3 , GeH_3 , etc.) with olefinic proton (3) is the determining factor in the preference of conformations I and II.

Another possible mode of interaction in these derivatives is of the intermolecular type, which has been proposed by a group of Russian workers for 1-(methylallyl)silane:¹⁶⁷



If intermolecular π bonding is present, there should be a noticeable concentration effect. In the present work, a sample of 3-silylpropene at a concentration of 90 v/v% in deuteriochloroform was prepared, analyzed and the data compared with that obtained for the 20% solution. The results are essentially identical, with a slight downfield shift of only $0.004\tau_{\text{SiH}_3}$ from the 20% to the 90% solution and slight upfield shifts for the olefinic protons. No significance is attached to these results.

D. The Attempted Preparation of Pseudohalogen Derivatives of Silylmethane

The most common organosilicon pseudohalides investigated are the cyanides, cyanates, thiocyanates and azides. If the pseudohalogen is to be attached directly to a silicon atom, the method usually employed is to allow a silicon halide to interact with a silver, ammonium or alkali metal salt of the desired pseudohalide. Some examples of the preparations

of pseudohalogen derivatives of silanes and organosilanes are presented in Table III-9.

Table III-9
Syntheses of Some Pseudohalogen Derivatives of Silane
and Organo Silanes

Silyl Compound	Pseudohalide	Product	Reference
SiH_3I	AgCN	SiH_3CN	126
$\text{CH}_3\text{SiH}_2\text{I}$	AgCN	$\text{CH}_3\text{SiH}_2\text{CN}$	70
$\text{R}_3\text{SiI}^{\text{a}}$	AgCN	$\text{R}_3\text{SiCN}^{\text{a}}$	57
$n\text{-C}_7\text{H}_{15}\text{SiCl}_3$	AgNCO	$n\text{-C}_7\text{H}_{15}\text{Si}(\text{NCO})_3$	7
SiH_3I	AgNCS	SiH_3NCS	126
$\text{CH}_3\text{SiH}_2\text{I}$	AgNCS	$\text{CH}_3\text{SiH}_2\text{NCS}$	70
$(\text{CH}_3)_2\text{SiHI}$	AgNCS	$(\text{CH}_3)_2\text{SiHNCS}$	122
$\text{R}_3\text{SiCl}^{\text{b}}$	NH_4SCN	$\text{R}_3\text{SiNCS}^{\text{b}}$	28
$\text{RSiCl}_3^{\text{c}}$	NaSCN	$\text{RSi}(\text{NCS})_3^{\text{c}}$	81
CH_3SiCl_3	NaN_3	$\text{CH}_3\text{Si}(\text{N}_3)_x\text{Cl}_{3-x}$	126

^a $\text{R} = \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7$
^b $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_4\text{H}_9$
^c $\text{R} = \text{CH}_2=\text{CHCH}_2, \text{CH}_2=\text{CH}$

Structural studies performed on some of the pseudohalogen derivatives of silane (Table III-10) are very interesting and have provoked much discussion. It would seem to be very interesting to determine the structure of the corresponding silylmethanes, where the pseudohalogen is separated from SiH_3 by a CH_2 group. It was therefore undertaken in the present research project to prepare these silylmethyl-halogenoids and thus make them available for such studies.

Table III-10

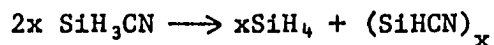
Structural Studies on Some Pseudohalogen Derivatives of Silane

Compound	Shape
SiH_3CN	Linear SiCN
SiH_3N_3	Bent NNN—Si
SiH_3NCO	Linear SiNCO ^a
$(\text{CH}_3)_3\text{SiNCO}$	Bent OCN—Si
SiH_3NCS	Linear SiNCS ^a
$(\text{CH}_3)_3\text{SiNCS}$	Bent SCN—Si

^a Bent from heavy atom skeleton from electron diffraction studies.¹⁷²

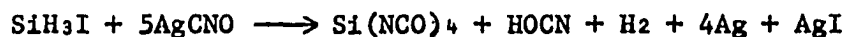
Previous successful reactions were used as models for the attempted reactions. For example, cyanomethyltrimethylsilane had been prepared by the reaction of sodium cyanide with chloromethyltrimethylsilane in DMSO.¹⁷³ Therefore, sodium cyanide was allowed to react with chloromethylsilane (and iodomethylsilane) in DMSO in the present work. The reaction of $\equiv\text{SiCH}_2\text{Cl} + \text{KCNS}$ in acetone is reported to produce $\equiv\text{SiCH}_2\text{SCN}$ ¹⁴¹ and thus this procedure was used in the reaction of $\text{SiH}_3\text{CH}_2\text{Cl}$ with KCNS. Unfortunately, these reactions did not yield the desired silylmethylhalogenoids. The success of silver pseudohalides with silyliodides (Table III-9) led us to try the system $\text{SiH}_3\text{CH}_2\text{I} + \text{AgX}$ ($\text{X} = \text{CN}, \text{CNS}$). This also failed to yield the desired products. However, silver cyanides previously had not reacted with chloromethyltrimethylsilane, even after 16 hours at 200°, ¹⁴⁷ so the failure of our reaction does not seem surprising.

MacDiarmid has found that silyl cyanide decomposes, probably according to the equation:¹²⁶



Decomposition was greatly increased by the presence of mercury. If $\text{SiH}_3\text{CH}_2\text{CN}$ formed in our reaction, it could have undergone a well known type of intramolecular rearrangement reaction to give $\text{CH}_3\text{SiH}_2\text{CN}$, which in turn decomposed, especially with the presence of mercury in the vacuum line. The thiocyanate could also undergo a similar reaction.

There is also a possibility that the Si-H bonds underwent attack by the metal salts, such as MacDiarmid found for SiH_3I and AgCNO :¹²⁶



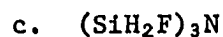
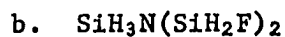
SUMMARY

The present research was conducted with the following three objects in mind:

1. To synthesize new and useful compounds of the germanium hydrides by using alkali metal derivatives of germane.
2. To investigate the selective fluorinating power of phosphorus pentafluoride with several silyl and organosilyl compounds.
3. To attempt to determine the presence or absence of interaction between the unoccupied d orbitals of a group IVB element and the p_{π} orbitals of a σ -bonded olefin by investigating the high resolution proton magnetic resonance spectra of $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$, $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ and $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$.

The goals were accomplished by performing the following experiments:

1. 1,2-Digermylethane was prepared in 45% yield by the reaction of solid NaGeH_3 with $\text{ClCH}_2\text{CH}_2\text{Cl}$ at room temperature.
2. 3-Germylpropene was prepared in 15% yield by the reaction of solid NaGeH_3 with $\text{CH}_2=\text{CHCH}_2\text{Br}$ at 0° .
3. 3-Fluorosilylpropene was prepared in 60% yield by the interaction of PF_5 and $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$ at -45° . 3-Difluorosilylpropene was obtained in a 6% yield from the same reaction.
4. Three derivatives of trisilylamine were prepared by the interaction of PF_5 with $(\text{SiH}_3)_3\text{N}$. The compounds were characterized as fully as the quantity of each compound permitted. The new derivatives were:
 - a. $(\text{SiH}_3)_2\text{NSiH}_2\text{F}$



5. The high resolution proton magnetic resonance spectra of $\text{CH}_2=\text{CHCH}_2\text{SiH}_3$, $\text{CH}_2=\text{CHCH}_2\text{SiH}_2\text{F}$ and $\text{CH}_2=\text{CHCH}_2\text{GeH}_3$ were analyzed by the computer program LAOCN 3.

The above experimental data led to the following conclusions:

1. Alkali metal derivatives of germane can be useful intermediates in the preparation of selected organogermanes if reaction conditions are properly chosen.

2. Phosphorus pentafluoride can be conveniently used to selectively fluorinate Si-H bonds in alkyl silanes and silylamines.

3. Fluorination by phosphorus pentafluoride of silanes or silylamines does not proceed if two or more electronegative groups are attached to silicon.

4. No evidence was found for the presence of inter- or intramolecular p-d interaction between the olefinic p_π orbitals and the empty d orbitals on silicon and germanium. The molecules were found to exist predominantly in the gauche conformation.

APPENDIXSYMBOLS AND ABBREVIATIONSINFRARED SPECTRA SYMBOLSIntensity Symbols

w = weak

m = moderate

s = strong

v = very

sh = shoulder

Assignment Symbols

ν_s = symmetric stretching

ν_a = asymmetric stretching

δ_s = symmetric deformation

δ_a = asymmetric deformation

ρ = rocking

s = scissors

t = twisting

w = wagging

ABBREVIATIONS

diglyme - bis (2-methoxyethyl)ether

DMSO - dimethyl sulfoxide

G.C. - gas chromatograph(ic)

HMPT - hexamethylphosphortriamide

monoglyme - 1,2-dimethoxyethane

TSA - trisilylamine

BIBLIOGRAPHY

1. Allred, A. L., J. Inorg. Nucl. Chem., 17, 215 (1961).
2. Allred, A. L. and Rochow, E. G., J. Inorg. Nucl. Chem., 5, 269 (1958).
3. Almenningen, A., Bastiansen, O., Ewing, V., Hedberg, K. and Troetteberg, M., Acta Chem. Scand., 17, 2455 (1963).
4. Amberger, E. and Boeters, H. D., Angew. Chem. Intern. Ed., 2, 686 (1963).
5. Amberger, E. and Mühlhofer, E., J. Organometal. Chem., 12, 55 (1968).
6. Anderson, F. A. and Bak, B., Acta Chem. Scand., 8, 738 (1954).
7. Anderson, H. H. and Hendifar, A., J. Org. Chem., 26, 3033 (1961).
8. Aulinger, B. J. and Reerink, W., Z. anal. Chem., 197, 24 (1963).
9. Aylett, B. J., Advan. Inorg. Chem. Radiochem., 11, 249 (1968).
10. Aylett, B. J. and Peterson, L. K., J. Chem. Soc., 4043 (1965).
11. Bailey, D. L. and Pines, A. N., Ind. and Eng. Chem., 46, 2363 (1954).
12. Bak, B., Bruhn, B. and Rastrup-Anderson, J., J. Chem. Phys., 21, 752 (1953).
13. Ball, D. F., Carter, T., McKean, D. C. and Woodward, L. A., Spectrochim. Acta, 20, 1721 (1964).
14. Beard, C. I. and Dailey, B. P., J. Am. Chem. Soc., 71, 929 (1949).
15. Becker, E. D., High Resolution NMR, Academic Press, New York (1969).
16. Bellama, J. M. and MacDiarmid, A. G., J. Organometal. Chem., 18, 275 (1969).
17. Bentley, F. F., Smithson, L. D. and Rozek, A. L., Infrared Spectra and Characteristic Frequencies ~700-300 cm.⁻¹, Interscience, New York (1968).
18. Birchall, T. and Drummond, I., J. Chem. Soc. (A), 1859 (1970).
19. Birchall, T. and Jolly, W. L., Inorg. Chem., 12, 2177 (1966).
20. Boberg, F., Winter, G. and Moos, J., Ann., 616, 1 (1958).
21. Booth, H. S. and Stillwell, W. D., J. Am. Chem. Soc., 56, 1531 (1934).

22. Bornhorst, W. R. and Ring, M. A., *Inorg. Chem.*, 7, 1009 (1968).
23. Bothner-By, A. A., Castellano, S., Ebersole, S. J. and Günther, H., *J. Am. Chem. Soc.*, 88, 2466 (1966).
24. Bothner-By, A. A., Castellano, S. and Günther, H., *J. Am. Chem. Soc.*, 87, 2439 (1965).
25. Bothner-By, A. A. and Naar-Colin, C., *J. Am. Chem. Soc.*, 83, 231 (1961).
26. Bothner-By, A. A., Naar-Colin, C. and Günther, H., *J. Am. Chem. Soc.*, 84, 2748 (1962).
27. Bovey, F. A., *NMR Data Table for Organic Compounds*, Interscience, New York (1967), vol. 1.
28. Brinckman, F. E. and Stone, F. G. A., *J. Inorg. Nucl. Chem.*, 11, 24 (1959).
29. Brockway, L. O. and Jenkins, H. O., *J. Am. Chem. Soc.*, 58, 2036 (1936).
30. Brockway, L. O. and Wall, F. T., *J. Am. Chem. Soc.*, 56, 2373 (1934).
31. Brook, A. G. and Wolfe, S., *J. Am. Chem. Soc.*, 79, 1431 (1957).
32. Brown, H. C., Bartholomay, H. and Taylor, M. D., *J. Am. Chem. Soc.*, 66, 435 (1944).
33. Brown, H. C. and Johnson, S., *J. Am. Chem. Soc.*, 76, 1978 (1954).
34. Brown, M. P., Okowara, R. and Rochow, E. G., *Spectrochim. Acta*, 16, 595 (1960).
35. Burg, A. B. and Kuljian, E. S., *J. Am. Chem. Soc.*, 72, 3103 (1950).
36. Bürger, H., *Monatsh. Chem.*, 97, 869 (1966).
37. Bürger, H., *Spectrochim. Acta*, 24A, 2015 (1968).
38. Buttler, M. J. and McKean, D. C., *Spectrochim. Acta*, 21, 485 (1965).
39. Buttler, M. J., McKean, D. C., Taylor, R. and Woodward, L. A., *Spectrochim. Acta*, 21, 1379 (1965).
- 39a. Campbell-Ferguson, H. J., Ebsworth, E. A. V., MacDiarmid, A. G. and Yoshioka, T., *J. Phys. Chem.*, 71, 723 (1967).
40. Castellano, S. and Bothner-By, A. A., *J. Chem. Phys.*, 41, 3863 (1964); LAOCN 3, Mellon Institute, Pittsburgh, Pennsylvania (1966).
41. Clark, H. C. and Poller, R. C., *Can. J. Chem.*, 48, 2670 (1970).

42. Cotton, F. A., Inorganic Syntheses, McGraw-Hill, New York (1972), vol. xiii, p. 66.
43. Cottrell, T. L., The Strengths of Chemical Bonds, 2nd ed., Butterworths London and Washington, D. C. (1958).
44. Cradock, S. and Ebsworth, E. A. V., *Chem. Commun.*, 57 (1971).
45. Cradock, S., Ebsworth, E. A. V., Davidson, G. and Woodward, L. A., *J. Chem. Soc. (A)*, 1229 (1967).
46. Cradock, S., Ebsworth, E. A. V. and Robiette, A. G., *Trans. Faraday Soc.*, 60, 1502 (1964).
47. Cradock, S., Gibbon, G. A. and Van Dyke, C. H., *Inorg. Chem.*, 6, 1751 (1967).
48. Craig, D. P., Maccoll, A., Nyholm, R. S., Orgel, L. E. and Sutton, L. E., *J. Chem. Soc.*, 332 (1954).
49. Crawford, V. A., Rhee, K. H. and Wilson, M. K., *J. Chem. Phys.*, 37, 2377 (1962).
50. Cross, R. J. and Glockling, F., *J. Organometal. Chem.*, 3, 146 (1965).
51. Cunliffe-Jones, D. B., *Spectrochim. Acta*, 21, 245 (1965).
52. Davidson, G., Woodward, L. A., Mackay, K. M. and Robinson, P., *Spectrochim. Acta*, 23A, 2383 (1967).
53. Dreyfus, R. M. and Jolly, W. L., *Inorg. Chem.*, 10, 2567 (1971).
54. Dushman, S., Scientific Foundations of Vacuum Techniques, Wiley, New York (1949).
55. Dutton, W. A. and Onyszczuk, M., *Inorg. Chem.*, 9, 1735 (1968).
56. Eaborn, C., Organosilicon Compounds, Butterworths, London and Washington, D. C. (1960).
57. Eaborn, C., *J. Chem. Soc.*, 2755 (1949).
58. Ebsworth, E. A. V., Volatile Silicon Compounds, Pergamon, London (1963).
59. Ebsworth, E. A. V. and Emeléus, H. J., *J. Chem. Soc.*, 2150 (1958).
60. Ebsworth, E. A. V., Frankiss, S. G. and Robiette, A. G., *J. Mol. Spectry.*, 12, 299 (1964).
61. Ebsworth, E. A. V., Hall, J. R., Mackillop, M. J., McKean, D. C., Sheppard, N. and Woodward, L. A., *Spectrochim. Acta*, 13, 202 (1958).

62. Ebsworth, E. A. V., Mould, R., Taylor, R., Wilkinson, G. R. and Woodward, L. A., *Trans. Faraday Soc.*, 58, 1069 (1962).
63. Ebsworth, E. A. V., Onyszchuk, M. and Sheppard, N., *J. Chem. Soc.*, 1453 (1958).
64. Ebsworth, E. A. V. and Turner, J. J., *J. Chem. Phys.*, 36, 2628 (1962).
65. Ebsworth, E. A. V. and Turner, J. J., *J. Phys. Chem.*, 67, 805 (1963).
66. Emeléus, H. J. and Kettle, S. F. A., *J. Chem. Soc.*, 2444 (1958).
67. Emeléus, H. J. and Mackay, K. M., *J. Chem. Soc.*, 2676 (1961).
68. Emeléus, H. J. and Maddock, A. G., *J. Chem. Soc.*, 293 (1944).
69. Emeléus, H. J. and Onyszchuk, M., *J. Chem. Soc.*, 604 (1958).
70. Emeléus, H. J., Onyszchuk, M. and Kuchen, W., *Z. anorg. allg. Chem.*, 283, 74 (1956).
71. Englehardt, G. and Kriegsmann, H., *Z. anorg. allg. Chem.*, 328, 194 (1964).
72. Finch, M. A., Marcus, L. H., Smirnoff, C., Van Dyke, C. H. and Viswanathan, N., *Syn. Inorg. Metal-Org. Chem.*, 1, 103 (1971).
73. Fishwick, M. and Wallbridge, M. G. H., *J. Organometall. Chem.*, 25, 69 (1970).
74. Fritz, H. P., *Chem. Ber.*, 94, 1217 (1961).
75. Garrity, S. P. and Ring, M. A., *Inorg. Nucl. Chem. Letters*, 4, 77 (1968).
76. Gibbon, G. A., Doctoral Dissertation, Carnegie-Mellon University, Pittsburgh, Pennsylvania (1968).
77. Gibbon, G. A., Wang, J. T. and Van Dyke, C. H., *Inorg. Chem.*, 6, 1989 (1967).
78. Glarum, S. N. and Kraus, C. A., *J. Am. Chem. Soc.*, 72, 5398 (1950).
79. Glidewell, C., Rankin, D. W. H. and Robiette, A. G., *J. Chem. Soc. (A)*, 2935 (1970).
80. Glidewell, C., Rankin, D. W. H., Robiette, A. G., Sheidrick, G. M., Beagley, B. and Cradock, S., *J. Chem. Soc. (A)*, 315 (1970).
81. Glowacki, G. R. and Post, H. W., *J. Org. Chem.*, 27, 634 (1962).
82. Gondal, S. K., MacDiarmid, A. G., Saalfeld, F. E. and McDowell, M. V., *Inorg. Nucl. Chem. Letters*, 5, 351 (1969).

83. Gondal, S. K., MacDiarmid, A. G., Saalfeld, F. E. and McDowell, M. V., *Inorg. Nucl. Chem. Letters*, 5, 413 (1969).
84. Goodrich, R. A. and Treichel, P. M., *J. Am. Chem. Soc.*, 88, 3509 (1966).
85. Gordy, W., *Phys. Rev.*, 69, 604 (1946).
86. Goubeau, J. and Jiménez-Barberá, J., *Z. anorg. allg. Chem.*, 303, 217 (1960).
87. Green, J. H. S., *Spectrochim. Acta*, 18, 39 (1962).
88. Gregor, I. K., *Aust. J. Chem.*, 18, 1485 (1965).
89. Gregor, I. K., *Aust. J. Chem.*, 18, 2035 (1964).
90. Gregor, I. K., *Aust. J. Chem.*, 19, 1977 (1966).
91. Griffiths, J. E., *J. Chem. Phys.*, 38, 2879 (1963).
92. Griffiths, J. E. and Onyszchuk, M., *Can. J. Chem.*, 39, 339 (1961).
93. Griffiths, J. E., Srivastava, T. N. and Onyszchuk, M., *Can. J. Chem.*, 40, 579 (1962).
94. Gross, B. and Forel, M-T., *J. Chim. Phys.*, 62, 1163 (1965).
95. Gutowsky, H. S. and Liehr, A. D., *J. Chem. Phys.*, 20, 1652 (1952).
96. Hayashi, M., Shimanouchi, T. and Mizushima, S., *J. Chem. Phys.*, 26, 608 (1957).
97. Hedberg, K., *J. Am. Chem. Soc.*, 77, 6491 (1955).
98. Hobgood, R. T., Goldstein, J. H. and Reddy, G. S., *J. Chem. Phys.*, 35, 2038 (1961).
99. Holmes, R. R. and Storey, R. N., *Inorg. Chem.*, 5, 2146 (1966).
100. Huggins, M. L., *J. Am. Chem. Soc.*, 75, 4123 (1953).
101. Isenberg, S., *Doctoral Dissertation, University of Chicago* (1937).
102. Jaffé, H. H., *J. Phys. Chem.*, 58, 185 (1954).
103. Jenkins, D. R., Kewley, R. and Sugden, T. M., *Trans. Faraday Soc.*, 58, 1284 (1962).
104. Jolly, W. L., *Synthetic Inorganic Chemistry*, Prentice Hall, Englewood Cliffs, New Jersey (1960).

105. Jolly, W. L., The Synthesis and Characterization of Inorganic Compounds, Prentice Hall, Englewood Cliffs, N.J. (1970).
106. Jolly, W. L., J.Chem.Educ., 44, 304 (1967).
107. Jolly, W. L., Inorg. Chem., 6, 1435 (1967).
108. Jolly, W. L., Inorg. Syn., 11, 113 (1968).
109. Jolly, W. L. and Drake, J. E., Inorg. Syn., 7, 34 (1963).
110. Jolly, W. L. and Norman, A. D., "Hydrides of Groups IV and V", in Preparative Inorganic Reactions, W. L. Jolly (Ed.), Wiley-Interscience, New York (1968), Vol. 4, p. 1.
111. Jones, R. G., Partington, P., Rennie, W. J. and Roberts, R. M. G., J. Organometal. Chem., 35, 291 (1972).
112. Kaesz, H. D. and Stone, F. G. A., J. Chem. Soc., 1433 (1957).
113. Kasai, P. H. and Myers, R. J., J. Chem. Phys., 30, 1096 (1959).
114. Kennedy, R. C., Freeman, L. P., Fox, A. P. and Ring, M. A., J. Inorg. Nucl. Chem., 28, 1373 (1966).
115. Kifer, E. W., Doctoral Dissertation, Carnegie-Mellon University, Pittsburgh, Pennsylvania (1968).
116. Kifer, E. W. and Van Dyke, C. H., Chem. Commun., 1330 (1969).
117. Kostelnik, R. J. and Wisosky, D. E., private communication.
118. Kozyukov, V. P., Sheludyakov, V. D. and Mironov, V., Zh.Obshch. Khim., 38, 1133 (1968).
119. Kraus, C. A. and Carney, E. S., J. Am. Chem. Soc., 56, 765 (1934).
120. Kraus, C. A. and Nutting, H. S., J. Am. Chem. Soc., 54, 1622 (1932).
121. Kriegsmann, H., Englehardt, G., Z. anorg. allg. Chem., 310, 320 (1961).
122. Kuchen, W., Z. anorg. allg. Chem., 288, 101 (1956).
123. Kuznesof, P. M. and Jolly, W. L., Inorg. Chem., 7, 2574 (1968).
124. Langer, H. G. and Blut, A. H., J. Organometal. Chem., 5, 288 (1966).
125. MacDiarmid, A. G., "Halogenoid Derivatives of the Silanes", in Preparative Inorganic Reactions, W. L. Jolly (Ed.), Wiley-Interscience, New York (1964), Vol. I, p. 165.
126. MacDiarmid, A. G., J. Inorg. Nucl. Chem., 2, 88 (1956).

127. MacDiarmid, A. G., *Quart. Rev. (London)*, 10, 208 (1956).
128. MacDiarmid, A. G., *Advan. Inorg. Chem. Radiochem.*, 3, 207 (1961).
129. Mackay, K. M., *Hydrogen Compounds of the Elements*, Spon, London (1966).
130. Mackay, K. M. and Watt, R., *J. Organometal. Chem.*, 6, 336 (1966).
131. Mackay, K. M. and Watt, R., *Spectrochim. Acta*, 23A, 2761 (1967).
132. Mason, R. and Russel, D. R., *Chem. Commun.*, 26 (1966).
133. McCusker, P. A. and Ostdick, T., *J. Am. Chem. Soc.*, 81, 5550 (1959).
134. Mironov, V. F., *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1884 (1962).
135. Muetterties, E. L., Bither, T. A., Farlow, M. W. and Coffman, D. D., *J. Inorg. Nucl. Chem.*, 16, 52 (1960).
136. Mulliken, R. S., *J. Am. Chem. Soc.*, 72, 4493 (1950).
137. Mulliken, R. S., *J. Am. Chem. Soc.*, 74, 811 (1952).
138. Mulliken, R. S., *J. Am. Chem. Soc.*, 77, 884 (1955).
139. Nakagawa, I. and Mizushima, S., *J. Chem. Phys.*, 21, 2195 (1953).
140. Newman, C., O'Loane, J. K., Polo, S. R. and Wilson, M. K., *J. Chem. Phys.*, 25, 855 (1956).
141. Noll, J. E., *J. Am. Chem. Soc.*, 77, 3149 (1955).
142. Onyszchuk, M., *Can. J. Chem.*, 39, 808 (1961).
143. Pauling, L., *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, N. Y. (1960).
144. Pemsler, J. P. and Planet, W. G., Jr., *J. Chem. Phys.*, 24, 920 (1956).
145. Ponomarenko, V. A., Zueva, G. Ya., Andreev, N. S., *Izv. Akad. Nauk SSSR*, 1758 (1961).
146. Pritchard, H. O. and Skinner, H. A., *Chem. Rev.*, 55, 745 (1955).
147. Prober, M., *J. Am. Chem. Soc.*, 77, 3224 (1955).
148. Quinn, H. W., McIntyre, J. S. and Peterson, D. J., *Can. J. Chem.*, 43, 2896 (1965).
149. Rankin, D. W. H., *J. Chem. Soc.*, 1926 (1969).

150. Rijkens, F. and Van der Kerk, G. J. M., Investigations in the Field of Organogermanium Chemistry, Schotanus and Jens Utrecht, N. V., Utrecht, The Netherlands (1964).
151. Ring, M. A. and Ritter, D. M., J. Phys. Chem., 65, 182 (1961).
152. Ring, M. A. and Ritter, D. M., J. Am. Chem. Soc., 83, 802 (1961).
153. Roberts, R. M. G., J. Organometal. Chem., 12, 79 (1968).
154. Roberts, R. M. G., J. Organometal. Chem., 18, 307 (1969).
155. Robinson, D. W., J. Am. Chem. Soc., 80, 5924 (1958).
156. Rondeau, R. E. and Hasrah, J., J. Mol. Spectrosc., 21, 332 (1966).
157. Rudakova, S. E. and Pentin, Yu. A., Opt. Spectry., 18, 339 (1965).
158. Rudakova, S. E. and Pentin, Yu. A., Opt. Spectry., 20, 353 (1966).
159. Rudakova, S. E. and Pentin, Yu. A., Opt. Spectry., 21, 240 (1966).
160. Rustad, D. S., Birchall, T. and Jolly, W. L., Inorg. Syn., 11, 128 (1968).
161. Rustad, D. S. and Jolly, W. L., Inorg. Chem., 6, 1986 (1967).
162. Rustad, D. S. and Jolly, W. L., Inorg. Chem., 7, 213 (1968).
163. Sadtler Research Laboratories, Sadtler Standard Spectra, Philadelphia, Pennsylvania (1968).
164. Sanderson, R. T., Vacuum Manipulations of Volatile Compounds, John Wiley and Sons, New York, N. Y. (1948).
165. Sanderson, R. T., J. Am. Chem. Soc., 74, 4792 (1952).
166. Sanderson, R. T., J. Chem. Phys., 23, 2467 (1955).
167. Saratov, E. and Reikhsfel'd, V. O., Zh. Obshch. Khim., 36, 2183 (1966).
168. Schaefer, T., Can. J. Chem., 40, 1 (1962).
169. Schmutzler, R., Inorg. Chem., 3, 410 (1964).
170. Schmutzler, R., Adv. Fluor. Chem., 5, 31 (1965).
171. Scott, D. W. and McCullough, J. P., J. Am. Chem. Soc., 80, 3554 (1958).
172. Sheldrick, G. M., Abstr. Chem. Soc./R.I.C. Meeting, Paper 7.6, Edinburgh, Scotland (1970).
173. Shiina, K. and Kumada, M., Mem. Fac. Eng., Osaka City Univ., 3, 195 (1962).

174. Shriver, D. F., The Manipulation of Air-Sensitive Compounds, McGraw-Hill, New York (1969).
175. Siebert, H., *Z. anorg. allg. Chem.*, 268, 177 (1952).
176. Smith, A. L. and Angelott, N. C., *Spectrochim. Acta.*, 15, 412 (1959).
177. Smith, F. B. and Kraus, C. A., *J. Am. Chem. Soc.*, 74, 1418 (1952).
178. Sommer, L. H., Citron, J. D. and Parker, G. A., *J. Am. Chem. Soc.*, 91, 4729 (1969).
179. Spangenberg, H. J. and Pfeiffer, M., *Z. Physik. Chem.*, 232, 343 (1966).
180. Steward, W. B. and Nielson, H. H., *Phys. Rev.*, 48, 861 (1953).
181. Stock, A. and Somieski, C., *Ber.*, 52, 695 (1919).
182. Stock, A. and Somieski, C., *Ber.*, 54, 740 (1921).
183. Stone, F. G. A., Hydrogen Compounds of Group IV Elements, Prentice-Hall, Englewood Cliffs, N. J. (1962).
184. Stone, F. G. A. and Seyferth, D., *J. Inorg. Nucl. Chem.*, 1, 112 (1955).
185. Sujishi, S. and Witz, S., *J. Am. Chem. Soc.*, 76, 4631 (1954).
186. Sujishi, S. and Witz, S., *J. Am. Chem. Soc.*, 79, 2447 (1957).
187. Sundermeyer, W., *Angew. Chem.*, 74, 875 (1962).
188. Teal, G. K. and Kraus, C. A., *J. Am. Chem. Soc.*, 72, 4706 (1950).
189. Treichel, P. M., Goodrich, R. A. and Pierce, S. B., *J. Am. Chem. Soc.*, 89, 2017 (1967).
190. Ulbricht, K. and Chvalovsky, V., *J. Organometall. Chem.*, 12, 105 (1968).
191. Urch, D. S., *J. Inorg. Nucl. Chem.*, 25, 771 (1963).
192. Van Dyke, C. H., Doctoral Dissertation, University of Pennsylvania, Philadelphia, Pennsylvania (1964).
193. Van Dyke, C. H., "The Silanes" in Kirk-Othmer Encyclopedia of Chemical Technology, A. Standen (Ed.), Wiley, New York (1969), Vol. 18, p. 172.
194. Van Dyke, C. H., "Inorganic Derivatives of Germane and Digermane" in Preparative Inorganic Reactions, W. L. Jolly (Ed.), Wiley, New York (1971), Vol. 6, p. 157.
195. Van Dyke, C. H., "Synthesis and Properties of the Silicon-Halogen and Silicon-Halogenoid Bond" in Organometallic Compounds of the Group IV Elements, A. G. MacDiarmid (Ed.), Marcel Dekker, New York (1972), Vol. 2, part 1.

196. Van Dyke, C. H. and Kifer, E. W., *Inorg. Chem.*, 11, 404 (1972).
197. Van Dyke, C. H. and MacDiarmid, A. G., *Inorg. Chem.*, 3, 747 (1964).
198. Van Dyke, C. H. and MacDiarmid, A. G., *Inorg. Chem.*, 3, 1071 (1964).
199. Varma, R. and Cox, A. P., *Angew. Chem.*, 76, 649 (1964).
200. Voronkov, M. G. and Dolgov, B. N., *Zh. Obshch. Khim.*, 24, 1082 (1954); *CA* 49, 8791 (1955).
201. Wang, J. T. and Van Dyke, C. H., *Inorg. Chem.*, 6, 1741 (1967).
202. Wang, J. T. and Van Dyke, C. H., *Inorg. Chem.*, 7, 1319 (1968).
203. Wannagut, U., Höfler, F. and Bürger, H., *Monatsh. Chem.*, 99, 1186 (1968).
204. Ward, L. G. L. and MacDiarmid, A. G., *J. Am. Chem. Soc.*, 82, 2151 (1960).
205. West, R., Whatley, L. S. and Lake, K. J., *J. Am. Chem. Soc.*, 83, 761 (1961).
206. Whipple, E. B., Goldstein, J. H. and McClure, G. R., *J. Am. Chem. Soc.*, 82, 3811 (1960).
207. Wiberg, K. B. and Nist, B. J., *J. Am. Chem. Soc.*, 83, 1226 (1961).
208. Williamson, M. P., Kostelnik, R. J. and Castellano, S. M., *J. Chem. Phys.*, 49, 2218 (1968).
209. Wilson, M. K. and Santiago, R. P., *J. Chem. Phys.*, 20, 1716 (1952).
210. Yamasaki, K., Kotera, A., Yokoi, M. and Ueda, Y., *J. Chem. Phys.*, 18, 1414 (1950).

INDEX

	<u>Page</u>
Acknowledgments	iii
Abstract	xii
Apparatus and Techniques	24
Bibliography	180
Criteria of Purity	35
Chemical Shifts	
of 1,1'-difluorotrisilylamine	104,167
1,1-digermylethane	59
1,2-digermylethane	50
germylmethyl methyl sulfide	76
3-germylpropene	132
3-monofluorosilylpropene	133
monofluorotrisilylamine	104,167
1,1',1'-trifluorotrisilylamine	104,167
Discussion	135
Figures, index	ix
Fractionation	24
Gas Chromatography	
collection trap	30
columns	31
inlet and collection systems	28
operation of	26
General aspects of group IVB elements	2
Infrared spectrum	
determination	34
of 3-difluorosilylpropene	90
1,1'-difluorotrisilylamine	100
1,1-digermylethane	58
1,2-digermylethane	49
germylmethyl methyl sulfide	74
3-germylpropene	67
3-monofluorosilylpropene	89
Introduction	1
Low temperature baths	33

Mass spectrum	
determination	35
of 1,1'-difluorotrisilylamine	106
1,1-digermylethane	60
1,2-digermylethane	53
germylmethyl methyl sulfide	78
3-germylpropene	66
3-monofluorosilylpropene	93
monofluorotrisilylamine	105
1,1',1''-trifluorotrisilylamine	107
Molecular weight determination	32
Phosphorus pentafluoride, reaction with	
3-silylpropene	83,153
1,1,1',1''-tetramethyldisiloxane	108,157
1,1,1',1''-tetramethyldisilylamine	107
trisilylamine	96,160
Potassium germyl, preparation	71
Preparation and properties	
of 3-difluorosilylpropene	83
1,1'-difluorotrisilylamine	96
1,1-digermylethane	55
1,2-digermylethane	41
germylmethyl methyl sulfide	71
3-germylpropene	62
3-monofluorosilylpropene	83
monofluorotrisilylamine	96
1,1',1''-trifluorotrisilylamine	96
Proton magnetic resonance spectrum	
determination	34
of 1,1'-difluorotrisilylamine	104
1,2-digermylethane	51,52
germylmethyl methyl sulfide	77
3-germylpropene	69,124
3-monofluorosilylpropene	94,95,123
3-silylpropene	117-122
1,1',1''-trifluorotrisilylamine	104
Reagents and starting materials	37
Sodium germyl, preparation	41
Summary	180
Table of contents	iv
Tables, index	v

Vapor pressure data	
determination	35
for 1,1'-difluorotrisilylamine	98
1,2-digermylethane	44
3-germylpropene	64
3-monofluorosilylpropene	85